INVESTIGATION OF CATALYTIC COMBUSTION OF IMPURITIES OF AIR

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SUMMARY

A catalytic coil consisting of parallel corrugated ribbons of chromel alternated with layers of asbestos coated with precious metal catalyst, constructed to provide straight-through channels for air passage, was used to oxidize carbon monoxide, hydrogen and methane, present as dilute (0.5%) impurities in air.

Platinum when applied to the asbestos was significantly inferior to palladium for the oxidation of methane, the most troublesome of the gases tested. In addition, the catalyst operating temperature was found to decrease with increasing surface concentration of palladium, with length of catalyst, and with decreasing channel size.

From this, a plan for an integrated air purification system including heat exchanger and insulation was developed, based on a laboratory tested catalyst. The system would weigh under 25 lbs (including power penalty of 0.3 lbs./watt), and should remove virtually all of the carbon monoxide and hydrogen from the air while leaving a residual of no more than 250 ppm of methane.

ABSTRACT

INVESTIGATION OF CATALYTIC COMBUSTION OF IMPURITIES IN AIR

A study was made of the catalyzed combustion of impurities in air. These studies included laboratory tests of several configurations of corrugated catalyst support to minimize air flow resistance and optimize catalyst length, two catalysts - platinum and palladium, and three impurities - hydrogen, carbon monoxide, and methane.

From these data, a conceptual design of a catalytic combustion system was derived, allowing calculation of the weight and power requirement of a system of optimal configuration.

INTRODUCTION

For this study, it was assumed that the metabolic production of methane (CH_4) is 5.4 grams/man-day, hydrogen (H_2) is 0.45 grams/man-day, and carbon monoxide (CO) is 0.3 grams/man-day. Assuming a cabin volume of 500 cu ft per man in a spacecraft, a daily buildup of 520, 350 and 17 ppm per day respectively, would result, if unchecked. Additional sources of air pollutants such as plastics and regenerative chemical systems would contribute increased quantities of these contaminants.

Some sort of air purifying device must be included in the space module to maintain proper health standards. Since all three contaminants are oxidizable, one of the simplest methods for accomplishing the task is the passage of the pre-heated contaminated air through a catalytically active pebble bed, followed by absorption of the resulting CO_2 and H_2O along with respiratory CO_2 and H_2O.

This report presents data on the effectiveness of a new type of catalytic combustion unit in removing the above-mentioned gases, along with operating conditions and weights for an integrated air purification system employing one of these catalyst units. The heart of the device consists of strips of asbestos coated with precious-metal catalyst alternated with corrugated chromel ribbon. The strips are wound into the form of a helix so that the corrugated metal affords straight-through channels for the passage of air while also serving as an electrical heater (see Fig. 1). The advantages of this device over a conventional pebble bed are four: first, the straight-through air passages produce a much smaller pressure drop across the catalytic structure; second, the use of the chromel ribbon as a heater in intimate contact with the catalyst itself cuts heat loss to a minimum and makes a more compact unit; third, the device is small and light; and last, the presence of many different oxidation catalysts in the forms of oxides of chromium, nickel, aluminum and silicon along with the precious metal itself enhances the effectiveness of the device in destroying mixtures of different gases, since no single catalytic material is best for the oxidation of all contaminants.

The relative ease with which carbon monoxide and hydrogen are oxidized by this device, when compared with methane removal, prompts an examination of the term "proper health standards" with respect to allowable methane concentration in the air. This becomes a factor in the overall weight of the unit, because the tolerance limit on methane in the

atmosphere is found to dictate the operating temperature of the catalyst, and this in turn is directly related to the heat loss of the system..Although carbon monoxide is a specific chemical asphyxiant and combines with hemaglobin, thereby excluding oxygen, medical indications (1) are that methane is a simple asphyxiant, producing its effects only by reducing the concentration of oxygen. Hence, a small but constant level of methane may be tolerable, whereas carbon monoxide must be removed to very low concentrations.

In light of these facts, a system built around a laboratory tested catalytic unit has been designed on paper, weighing 24.7 lbs total (including the power penalty of 0.3 lbs/watt), which will remove essentially all the carbon monoxide and hydrogen passing through it and will allow a residue of no more than 250 ppm (0.025% by volume) of methane to remain in the exit stream.

EXPERIMENTAL

Catalytic Coil Detail

Configuration. - All catalytic coils tested in performance of this contract had the same exterior dimensions (Fig. 1). They were 2" in length, 2" in diameter, and contained 3/4" diameter ceramic cores. Early tests were made on single catalytic coils. In later experiments four coils in series were used to obtain a larger volume of catalyst.

There was some variation between the single and multiple coils in their internal structure to insure a reasonably flat axial temperature profile for the single coils. In these, 5 mil chromel ribbon, 1/4" wide, was used in series with 5 mil ribbon, 1" wide. The narrower ribbon, which dissipated 80% of the power, was situated at the air inlet end of the coil for rapid heating of the air, which was essential, due to the short length of the coil. Both ribbons were wound with the asbestos over the entire helical path of the coil, so that a cross-sectional view in the plane of the axis of the coil would disclose the two corrugated ribbons of unequal width lying side by side on the asbestos. The chromel was extended slightly beyond the front and rear edges of the asbestos in order to prevent feathering or distortion of the asbestos and subsequent blocking off of some of the air passages.

Because of its much greater length, it was not necessary to take the above precaution for rapid initial heating in the four-coil catalytic structure. Each of the four coils contained two 1/4" wide 2 mil ribbons and one 1/2" wide 3 mil ribbon, all electrically in series, and with the 1/2" ribbon in the middle. The higher resistance of these coils (11 ohms each as opposed to 2.3 ohms for the single coils) allowed them to be run directly off a Variac without the aid of a transformer, when the tandem was connected together.

The dimensions of the corrugations on the metal were varied during the course of experimentation on single coils to study the influence of this parameter on the efficiency of oxidation of the gases (see Table 1). With regard to this table, corrugations per inch refers to the number of full "sine waves" which occur in 1" of the material after it has been corrugated. It can be seen that when the metal is placed between two sheets of asbestos, two channels are formed for every full sine wave. The amplitude of the corrugation is the distance between adjacent sheets of asbestos. The number of layers refers to the number of concentric open areas which can be counted on the face of the coil for a given corrugation.

For the tandem unit, only the last or finest corrugation size was employed.

Instrumentation. - During single unit experimentation, #28 chromel-alumel thermocouples were spot-welded directly to the chromel ribbon in order to monitor surface temperatures within the catalytic coil. Four thermocouples, two on the inlet or 1/4" wide ribbon, and two on the outlet or 1" wide ribbon were used to establish a radial as well as a transverse temperature profile. Radially, for the initial coil tested (9.5 corr./in.) additional thermocouples were welded to the chromel at the third and seventh layers from the center. For the second coil (15 corr./in.), the thermocouples were welded at the fourth and ninth layer. For the last and finest coil (20 corr./in.) the thermocouples were welded at the fourth and twelfth layers. Corresponding thermocouples on the inlet and outlet ribbons were put in the same sector of the same layer. Care was taken that the thermocouple wires did not block the air passage in which they were welded, since this would cause overheating in that section and an erroneous reading.

Processing of coils. - Since asbestos paper contains a certain percentage of organic matter which burns off during initial heating, the coils were "cured" after they have been inserted into the reactor by energizing the coils and flushing away the resulting smoke with a low air flow lest this smoke

later interfere with testing. This curing process takes approximately 1/2 hr.

The precious-metal catalytic material in the form of an unfluxed suspension of powder in drying oil is applied to both sides of the asbestos paper before the strips are wound into a coil. The concentration of metal powder can be controlled rather well by striving for a uniform degree of dark color on the asbestos paper. Curing of a coil containing precious-metal catalyst takes somewhat longer than that of a simple chromel-asbestos coil in order to dispel the suspension vehicle from the asbestos. Palladium (Pd) and platinum (Pt) have been applied separately to the asbestos for testing in the course of this contract.

Integrated Testing System

The reaction tube itself is a 2 ft long section of Vycor glass of approximately 2" I.D., having 75/50 ball joints at either end (see Fig. 2). The tube is wrapped with 1" magnesia insulation. Attached to each ball joint is an 8" section of Pyrex glass with an O-ring joint and a side-arm for gas or air transmission. Through small holes in 1/8" thick Transite sheets clamped against each O-ring, thermocouples and power leads are fed to the catalytic unit. RTV, a silicon rubber sealant, is used to seal the wires in the Transite sheet. All glass joints in the system are clamped and coated with high vacuum silicone grease to insure a leak-free system. Two side-arms, fitted to the airstream line for sampling purposes, are placed sufficiently far from the catalyst so that both upstream and downstream sampling is done essentially at room temperature. Gas samples are drawn from the test system through a three-way stopcock directly to a chromatograph by means of a vacuum pump connected downstream from the chromatograph sampling chamber. The chromatograph is an F+M Model 700 instrument with metal sampling valves and a thermal conductivity detection system.

In addition to the previously mentioned thermocouples welded to the chromel ribbon within the catalytic coil, a ceramic jig within the Vycor tube supported three more thermocouples spaced radially in the airstream at a position 1/2" downstream from the catalytic unit. These thermocouples were protected by aluminum radiation shields and were mounted so as to give a radial temperature profile of the airstream inside the reaction tube. All seven thermocouples were connected to a terminal board and a multi-position switch, and the output from the switch was fed to a millivolt meter calibrated to read temperature directly. Tri-flat flowmeters, placed upstream from the catalytic unit, were used to monitor the flow of gas through the system.

Sampling Technique

The system was first brought to equilibrium with a flow of pure air, and then switched to the impurity source. Samples extracted downstream from the catalyst were obtained quickly thereafter. This method avoided the non-equilibrium problem created by the exothermic oxidation of the gases which would gradually increase the temperature of the system as the reaction progressed. Since the rate of this temperature increase would be related to the concentration of the impurity being oxidized, extension of the results to other concentrations would not be truly accurate. The results presented here represent true surface temperatures within the catalytic coils irrespective of impurity concentration.

Different flow rates (tests were made at 0.11, 0.22 and 0.33 CFM) created different temperature profiles within the single coil. Increased flow caused the front chromel ribbon to become cooler with respect to the rear one. For this reason, in plotting coil temperature (T_{coil}) against percentage oxidation of the gases, T_{coil} was not always given by the same thermocouple, but rather by the highest-reading thermocouple within the coil for that experiment. Generally this was the inner thermocouple on either the front or rear strip. Variac adjustment usually kept the temperature difference between these two points within $\pm$ 15°C. Radial variation was generally about 40°C, but this could probably be improved by better insulation.

Exit air temperature (referred to as T_{air}) was plotted as a single point vs. per cent gas removal, but actually was an average of the three temperatures recorded downstream from the catalyst.

During all experimental runs, upstream samples first were taken to normalize the amount of impurity which was entering the catalytic coil. Nitrogen, evident as a separate peak on the chromatogram, was used as an internal standard on all runs, i.e., adjustment was made on the magnitude of each impurity by first comparing its particular nitrogen peak with the normalized one and then increasing or decreasing the impurity level to match. Such adjustments rarely exeeded 2%. The modified area on the chromatogram was then compared with that obtained on the input sample to obtain percentage oxidation of the impurity. The areas under all chromatogram curves were determined through the use of a planimeter.

The gas impurities, CO, H_2 and CH_4, were obtained individually premixed with air in cylinders to specific concentrations of 500 and 5000 ppm. This made mixing unnecessary and eliminated variations of input from run to run.

Although it originally was proposed to perform experiments with a structure made of silicone carbide, this was not available from the manufacturing source and so the experiments could not be done.

RESULTS

Evaluation of internal parameters based on single coil tests. - Experiments were carried out on a catalytic coil with basic dimensions of 2" diameter and 2" length, but with internal variations which included change of catalytic material, change of catalyst loading, different size of individual straight-through channels, and air flow rate. The effectiveness of the various coils was tested on small percentages of CO, CH_4 and H_2, both separately and mixed. From the data, 18 curves of oxidation efficiency vs. both air and coil temperature are presented in sets of three's, corresponding to the three flow rates employed (Figs. 3A to 8C). For easy comparison of similar data points, Tables 2 through 7 may be used. In addition, several data points will be referred to which are not otherwise recorded in the text. The bulk of the presentation will be seen to stress methane oxidation, since this proved to be by far the most severe test for the catalytic unit.

A comparison made among any single set of figures (e.g., 3A, 3B and 3C) on oxidation efficiency shows that the air-to-coil temperature differential decreased as the air flow increased. This would indicate flow of a laminar type within the coil, since an increase in flow rate would induce more turbulence and therefore bring about better heat transfer to the air. Reynolds numbers calculated for the various coils, assuming flow through round tubes rather than the actual sinesoidal pattern presented, were well within the laminar region, being approximately 10-30. Even considering the error introduced through the geometric assumption made, the calculations are so far from the turbulent region it is difficult to believe that the flow can be other than laminar.

Further examination of the flow rate factor reveals the curious fact that with the singular exception of the 9.5 corr./in. unit the coil temperature for a specific percentage conversion remains fairly constant with respect to air flow, at least for the rates tested. (Compare flow data within Tables 2, 3, 4 and 6.)

The data collected (Figs. 3A-8C) can be used to examine the importance of the relationship of length to diameter for a given catalyst volume. Consideration of flow rate in terms of CFM/in.^{2} of catalyst frontal area enables one to

accommodate any rate without altering the flow characteristics by proper scaling of the catalyst diameter. Thus, 0.1 CFM through a 1" diameter unit would have the same amount of turbulence and contact time within the catalyst as 0.4 CFM through a 2" diameter system.

For the case at hand, the experimental data on methane at 0.11 CFM also applies to 0.33 CFM through a unit with three times the cross-sectional area (but the same length) and therefore three times the volume of the experimental model. Similarly, the experimental data on methane at 0.33 CFM through the same 2" unit may be extrapolated, since it is a first order reaction, to obtain results on a 6" long unit (see Appendices A and B). Therefore, data can be compared on two catalysts of equal volume carrying gas at the same flow to determine the more advantageous ratio of length to diameter.

From Appendix B, the coil temperature corresponding to a specific percentage removal of methane by the long narrow catalyst would be significantly lower than that of the short, large cross-section unit, although the contact times are equal. Referring to Table 8, if a single coil is 50% efficient, three coils would be 87.5% efficient, and if a single coil is 60% efficient, three coils will be 94% efficient. However, the better heat transfer occurring in the faster flowing coil when extended to 6" would undoubtedly bring the air temperature to equilibrium with the coil temperature. In the final analysis, power consumption by the unit must be measured in terms of the temperature of the air leaving the unit.

The difference between the two geometries is shown in Figs. 3 to 8, by comparing, for example, the coil temperature for a 60% removal at 0.33 CFM (since this would approximate the air temperature for a 94% removal in the long unit) with the air temperature for a 94% removal at 0.11 CFM, using consistent curves. Where coil temperatures are not listed for the 60% removal at the high flow rate, the low flow coil temperature may be substituted since, as it has already been stated, the coil temperature does not vary much with mass flow. Judging from this comparison, the more efficient unit would seem to be the short, large cross-sectional area unit.

However, for this particular installation where a heat exchanger would be used in conjunction with a catalyst, it is obvious that regardless of how short a contact time is employed, the air temperature would eventually establish itself at the coil temperature through feedback by the heat exchanger. Therefore, from this aspect, operating the coil at as low a temperature as is possible will produce the best results. This corresponds to the long narrow unit with the better heat transfer.

The influence of corrugation size within the unit may be seen by comparing similar flow rates and catalyst loadings in Tables 2 vs. 4 and 5 for methane and in Tables 6 vs. 7 for CO removal. The improvement of coil operation due to the combination of increased area of exposed catalyst (Table 1) and of more intimate contact of air with the surface is quite evident. The average decrease in coil temperature between the 9.5 corr./in. model and the 20 corr./in. model for comparable flows and percentage conversions is over 100°C. Although the decrease in channel size does correspond to an increasing pressure drop across the unit, this is relatively unimportant since even at an air temperature of 380°C and a flow of 0.33 CFM through the finest corrugation, the pressure drop was only 0.15" of water.

The most effectual parameter of all, however, has been the type and the surface concentration of the catalyst itself. The initial runs made under this contract were with a catalyst having 9.5 corr./in. and no precious metal applied to the asbestos. The only catalytic effect was derived from oxides of chromium and nickel present in the metal and of silica and alumina in the asbestos. No thermocouples were welded to the metal; however, a jig placed downstream from the unit did register air temperatures leaving the unit. Some indication of the poor efficiency of this unit may be seen in Table 9. The activation energy for CO was found to be 15 Kcal/mol (Appendix A). It was a first order reaction.

A similar coil instrumented with thermocouples and still without precious metal catalyst was used to oxidize hydrogen and methane. Some of these results also appear in Table 8. Oxidation was so difficult for these gases that it was not deemed profitable to accumulate enough data to determine activation energies.

The data points in Table 9 can all be compared with a single graph, Fig. 9, which presents the oxidation of H_2, CO and CH_4 on a coil of similar construction but having the asbestos surface coated with finely-divided palladium. This graph brings out not only the vastly improved operation of the unit with the precious metal catalyst, but also the relative difficulty still associated with methane removal.

Palladium was employed for the bulk of the experimentation, being used at a constant surface density of 1.2 mg/in.^{2} with each of the three different corrugation sizes. As previously stated, better results were produced as corrugation amplitude decreased. Oxidation of CO and CH_4 were first-order reactions having activation energies of 10.7 and 15.8 Kcal/mol. With the 9.5 corr./in. H_2 oxidation

was somewhere between first and second order. Its activation energy was not pursued since it obviously does not pose a major problem.

To determine whether any interference with CH_4 oxidation by the catalytic unit would be encountered from a simultaneous exposure to either CO or H_2, each of these latter gases was mixed with CH_4 and run at conditions sufficiently severe to totally destroy it. The resultant corresponding oxidation of CH_4 was consistently in line with the expected degree of removal, proving that there would be no interfering effects.

In addition, a heavier coating of 6 mg/in.^{2} of palladium was applied to the 15 corr./in. unit (Table 3 and Figs. 4A, 4B and 4C), which for similar conversions decreased T_{coil} by approximately 40°C below that necessary in the lightly palladized unit (Table 4). The heavier coating, therefore, becomes a valuable tool in lowering the overall operating temperature of the unit.

Platinum, the other precious metal catalyst tested, proved quite disappointing when applied at 1.40 mg/in.^{2} (essentially the same as for palladium) and used in conjunction with a 15 corr./in. coil. At a T_{coil} of 540° and a T_{air} of 385°, it removed only 15% of methane (5000 ppm input) when operating at 0.22 CFM. Similarly, at a T_{coil} of 630° and a T_{air} of 440°, only 30% was removed. However, when hydrogen was tested at this same flow rate, combustion was complete at a T_{coil} of 190° and a T_{air} of 170°C. Therefore, Pt, at least in the form used here, is significantly inferior to Pd. The effectiveness of the Pt on hydrogen did show that no mistake had been made in the application of the catalyst.

Scale-up of catalyst volume. - Based on the best results obtained on the individual catalytic coils, a system comprising four identical 2" units in series, each with chromel ribbon at 20 corr./in. and a Pd coating of 3.5 mg/in.^{2} was constructed. The solid line in Fig. 10 shows the methane oxidation efficiency of this unit as a function of air outlet temperature at a flow rate of 0.4 SCFM. As would be expected, the operating temperatures of this catalyst are far below that of the single coils.

For this unit thermocouples were not welded to the chromel itself. Since there are twelve separate ribbons within the system, such instrumentation would prove to be a very difficult task. Another approach was taken. For a single coil with 20 corr./in., in the range of 300 to 400°C, the differential of T_{coil} to T_{air} was about 80°C with the 2" contact length

when the flow rate was 0.33 CFM. With the added value of mixing gained from a rate of 0.4 CFM the air would certainly be in equilibrium with the coil after 8" of contact. Therefore, three thermocouples placed in the air stream at the catalyst outlet were the means of measuring the system temperature.

It is believed that this system although comprised of four 2" coils in series actually acts as a 6" unit with a preheater because the initial unit was too cold to be of much catalytic value. The air is introduced at room temperature and the chromel coils within the longer unit are not designed for rapid heating of the air as were the single coils in the earlier experiments. So, for an outlet air temperature of 350°C from the 8" unit, the coil temperature in the first unit would be about 290°C and the air at that point about 80° lower.

The most logical way to check such an idea would be to extrapolate the efficiency of a single unit at these temperatures to see whether 3 or 4 units in series would better approximate the efficiency of the present system. Unfortunately, no single coils were designed with the combined superior features of the tandem unit. However, if it may be assumed that since an increase of five times the Pd concentration on the 15 corr./in. unit lowered T_{coil} by about 40°C (Tables 3 vs. 4), then a threefold increase of the Pd concentration on 20 corr./in. unit would lower the T_{coil} by about 25°C, a comparison may be made.

If all four coils in the tested model are functioning, a 95% conversion taking place in the long unit (T_{air} is 415°C) would correspond to 50% removal through a single coil with the heavy Pd loading. However, if only three coils were operational, this would represent 60% removal in one unit. Adding the 25°C mentioned above to bring the operating temperature (440°C) in line with the lightly palladized single coil unit which was tested would result in a 59% removal. This value corresponds more closely to a three coil or 6" catalyst. Obviously at lower temperatures this comparison would be equally valid since the front coil, being colder, could only function more poorly.

Further reference to this unit will be as a 6" long model since the proposed integrated system will employ a heat exchanger. As a result, a more uniform temperature will exist within the catalytic unit, eliminating relatively inefficient areas.

DEVELOPMENT OF AN INTEGRATED SYSTEM CAPABLE OF HANDLING A 1 CFM THROUGHPUT

Dimensions. - As previously mentioned, the flow characteristics through a 2" diameter system at any given rate may

be matched to a 1 CFM flow rate through an appropriately scaled-up cross-sectional area. The tandem system described in the last section running at 0.4 SCFM carries 0.163 SCFM/in.^{2} of frontal area of catalytic coil. (For this calculation the area of the ceramic core has been subtracted out.) On this basis the same curve for efficiency of oxidation vs. temperature (Fig. 10) would apply to a unit the same length passing 1 CFM whose cross-sectional area was 6.14 in.^{2} Assuming that this unit had the same ceramic core as the present one, the new coil would have to be 2.9" in diameter.

It has already been stated that the oxidation of methane is a first order reaction. A projected performance curve based on actual data obtained for the four coil system is presented as the dotted line in Fig. 10. It corresponds to a unit having twice the length of the tested model. This extrapolation was carried out with the idea that running the reaction at a lower temperature in a longer chamber might be beneficial in minimizing the total system.

Operating temperature. - Fig. 9 indicates the large amount of energy necessary to oxidize CH_4 as opposed to CO and H_2. It is evident from this graph that combustion of the latter gases is essentially complete at 33% removal of CH_4. Although these curves do not represent the best catalyst configuration tested, the gross comparison does carry over. For this reason, the operating temperature of the catalyst (and therefore the weight of the system) will be controlled by the limitation placed on the allowable concentration of methane in the atmosphere. Along these lines medical reports indicate that methane is harmful only in proportion to its exclusion of oxygen from the body. The main problem in such an enclosed volume as a space capsule would then be its explosive limit, 5.53%. The system offered here would operate about two orders of magnitude below that, 0.025% methane by volume, allowing a 250 ppm residual.

The oxidation of methane is an exothermic reaction, generating 210.8 Kcal/g. mol. For the catalytic combustion unit operating at 1 SCFM, continual oxidation of 300 ppm methane would increase the air temperature by approximately 10°C. (This figure is given merely as a guideline.) If the unit were run at a temperature causing a relatively low percentage of methane conversion, the concentration of methane would naturally increase until even a low percentage conversion rate would result in a reasonable temperature increase. This temperature increase would likewise cause an increase in the efficiency of the oxidation, which in turn would produce a further temperature increase. In short, there would be a certain minimum temperature at which the catalytic unit may be run at which the

oxidation of methane is self-sustaining insofar as allowing no more than a specified residual percentage of methane to leave the catalytic coil.

Determination of this temperature will now be developed. The reciprocal of the slope of the solid curve in Fig. 10 may be thought of as the rate of change of temperature necessary to increase the efficiency of oxidation at the particular temperature where the slope is taken.

Similarly, on a plot of methane oxidation vs. temperature increase produced by the oxidation (based on the 10°C rise/300 ppm) the reciprocal of slopes of constant methane residual curves would indicate the rate of change of temperature produced at a given per cent conversion. Naturally, the slopes at given per cent removal would vary with allowable residual.

Clearly, the percentage removal at which the rate of heat production exceeds the rate of temperature increase necessary to extend the oxidation efficiency establishes the temperature at which the coil may be run to maintain a given residual. This temperature will increase with diminishing residual.

These minimum operating temperatures are calculated for allowable residuals between 100 and 1000 ppm for both the 6" and 12" models in Appendix C. The results appear in Fig. 14. The longer coil would operate between 20 and 40°C cooler than the other, depending upon allowable residual.

Design. - The most critical part of this development is the minimization of heat loss through the insulation against the weight of insulation. An equation based on a somewhat simplified model of the proposed 1 CFM unit was developed. For the calculation the reactor was assumed to be a cylinder (which it is), but hemispherical ends were placed on it to simulate the pipes entering and leaving the system. For the sake of symmetry in the calculations, the heat exchanger was left off this preliminary investigation. The equation itself sums the weight of the insulation as two parts, cylinder and hemisphere, plus the power loss, also divided into two components and rendered in terms of lbs/watt. The equation used is as follows:

$$\rho \left[\frac{4/3\ \pi R^3 + \pi L(R^2 - R_o^2)}{1728} \right] + 0.3 \left[\frac{\frac{\Delta T}{\ln R/R_o}}{2\pi L\ k} + \frac{\Delta T}{\frac{1}{R_o} - \frac{1}{R}} \right]$$

R_o = radius of catalyst

L = length of catalyst

R = outer radius of insulation

Min-k 1301, a Johns-Manville product with a density (ρ) of 10 lbs per cu ft and a thermal conductivity of 0.23 BTU-inch per hr-degree F-sq ft, was chosen as the insulation. The diameter of the catalyst was taken as 3.0" and the function was minimized for units both 6" and 12" in length at various operational temperatures corresponding to specific methane residuals. It was found that for operating temperatures in the range of 290°C to about 400°C that the minimum combination of heat loss and insulation weight occurred in the vicinity of 2" of insulation for both the 6" and 12" catalyst. The weight heat loss combination is plotted against allowable methane residual in Fig. 15 for both 6" and 12" systems.

As would be expected, this minimum weight combination increased with increasing operating temperature. However, for a given efficiency of operation with respect to oxidation of methane, the shorter coil consistently produced a smaller weight-heat loss combination than the longer unit, although always operating at a higher temperature. This, of course, is due to the difference in total surface area available to conduct heat away from the reactor. The 6" unit was therefore chosen, with a residual at 250 ppm methane. The operating temperature is 350°C which corresponds to a 60% conversion. Under these conditions, carbon monoxide and hydrogen are essentially completely oxidized so that the use of the reduced temperature in no way interferes with or limits their oxidation. Similarly, existence of 250 ppm or .025% by volume of methane in the air presents no health hazard whatsoever.

Air Preheater Co., with whom we consulted for a heat exchanger for the above system, designed a countercurrent recuperator based on a zero heat loss from the exchanger and an input temperature of 350°C. The unit was optimized with respect to recoverable heat vs. total weight of exchanger. The physical characteristics of their heat exchanger include dimensions of 17" x 1" x 1", an efficiency of 92.4%, an exchange temperature of 325°C (returning to the catalytic unit), a weight of 4.02 lbs, and a pressure drop of 0.74" H_2O on each side of the unit.

For our use the exchanger would be "folded" into thirds, producing a unit approximately 6" x 3" x 1". The addition of elbows would increase the weight to about 4.2 lbs and produce a total pressure drop of 1.6" H_2O. The corresponding make-up heat to the catalyst is 14.7 watts or 4.4 lbs.

The two major parts of the system, heat exchanger and catalyst now have the same length (6") and the same width (3"). Placing them side by side and with their long axes parallel and packing with the same 2" of insulation would produce a geometry shown from several angles in Fig. 16. The heat loss for this combination would then be about the same as for the original simplified case (since the insulation is the same thickness). The new weight of the combination is given by the increased volume of insulation necessary to cover the system. This calculates to be 0.287 ft^3 as opposed to 0.209 ft^3 previously. For Min-k 1301, this corresponds to a weight increase of 0.78 lbs. Thus, for an allowable residual of 250 ppm methane the insulation weight-heat loss combination would be 9.52 lbs.

The weight of the catalytic unit itself, 6" long and 3" in diameter, including the ceramic core, the self-contained heater and a 16-gage stainless steel container for the unit would be approximately 2 lbs. Based on the expected rate of methane production in terms of maximum heat which might be generated within the catalyst, the proposed reduced temperature at which the unit would run and the ability of this catalytic unit to withstand high temperatures, the use of an electric control to regulate the power input to the system seems unwarranted. Exclusion of such a device would eliminate a possible malfunction and also save weight.

The pressure drop across the entire system including catalytic coil and heat exchanger will be about 2.0" H_2O at operating temperature. This corresponds to a weight penalty of 0.35 lbs.

The frame for the system made of 20 gage stainless steel and based upon the surface created by placing 2" insulation around the heat exchanger catalyst combination (2.61 ft^2) would weigh 4.1 lbs. In all, the system proposed would weigh 24.68 lbs (see Table 12 for tabulated breakdown) and have dimensions of 13" x 7" x 8" (see Fig. 16 for a more complete description of the geometry).

CONCLUSIONS

1. The use of active Pd greatly enhances the operating conditions of the coils in the removal of CO, H_2 and CH_4.

2. The surface concentration of the Pd is similarly important.

3. Active Pt while quite effective on H_2 oxidation was found significantly inferior to Pd in removing CH_4.

4. The use of smaller openings in the straight-through channels was beneficial in reducing the operating temperature of the system.

5. The oxidation of CH_4 was first order. It was therefore possible to extrapolate the effectiveness of a longer unit from the performance of a smaller model.

6. A unit may be built weighing under 25 lbs which removes substantially all the CO and H_2 while leaving a residual of no more than 250 ppm CH_4 in the atmosphere.

RECOMMENDATIONS

In view of the results obtained under this contract, it is suggested that a prototype of the integrated device, including heat exchanger, be assembled and tested by Prototech Company.

Prototech Company
Division of Bolt Beranek and Newman, Inc
Cambridge, Massachusetts, June 30, 1967

APPENDIX A

Determination of Activation Energies

In order to determine the activation energy, the Arrhenius equation was assumed to be valid for the system under investigation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

k = reaction const.

E_a = activation energy

$\ln A$ = constant of integration

As can be noted in the above, if a reaction constant can be measured and a plot of ln k vs. the reciprocal of the reaction temperature constructed, one should obtain a straight line, the slope of which will be related to the energy of activation of the reaction (2).

The volume per minute flow of reactant gas at room temperature was corrected to correspond to air temperature in the reactor. Then from the known volume of the catalyst, a contact time or reaction time was calculated. Assuming first order reaction kinetics and utilizing data on per cent reactant remaining, reaction constants at various catalyst coil temperatures were calculated. If a plot of ln k vs. $1/T$ results in a straight line, this establishes the assumption of first order reaction kinetics.

Figs. 11 and 12 show sample curves for activation energy of CO and C_2H_4 oxidation through the 9.5 corr./in. unit with 1.2 mg/in.^{2} Pd applied to the asbestos. Both of these reactions were found to be first order. Similar calculations on H_2 disclosed its order to be somewhere between first and second.

APPENDIX B

Extrapolation of Catalyst Length

The interpretation of a first order reaction is that for a given temperature, flow rate and contact times a specific percentage of the gas will be oxidized regardless of concentration. Once a reaction has been categorized as first order, the effectiveness on the reactant of a longer catalyst length (greater contact time) is easily calculated. If a given length of catalyst will convert X per cent of a substance, then an equal length of catalyst placed behind the first will convert an equal per cent of what remains for an overall destruction of $X + X(100-X)$ per cent. For $\underline{n}$ units placed in series, the per cent removal becomes

$$\sum_{k=0}^{n-1} X(100-X)^k$$

Table 8 demonstrates the usefulness of 2, 3 and 4 coils in series, based on the achievement of a single unit. Applying this to a specific curve of oxidation efficiency vs. coil temperature enables one to determine either the increased efficiency of a longer unit at that temperature or the lower temperature at which the longer unit would accomplish the same task.

APPENDIX C

Method for Obtaining Design

Rather than become involved in a series of graphical differentiations of the curves of efficiency of oxidation vs. temperature and efficiency vs. temperature increase at varied residual outputs to obtain the minimum operating temperatures, another approach is taken. Fig. 13 is a graph of percentage removal vs. ppm input of methane. Lines of constant methane residual appear on the graph, indicating the extent to which oxidation must occur for a given input. These are crossed with lines of constant enthalpy produced by the oxidation expressed in terms of corresponding temperature rise of air. It should be noted that this is a completely general graph and is independent of flow rates.

The points of interest on this plot appear where the temperature lines cross a given residual curve. Thus, it can be seen for 100 ppm residual at a 76% conversion there is a 10° rise in temperature, and an 85% conversion produces an increase of 20°. This is essentially saying that a 76% conversion of 400 ppm could be accomplished if the temperature of the coil were 10° cooler and an 85% conversion of 720 ppm would take place even if the coil were 20° cooler.

Returning to Fig. 10, the performance curve for the four coils in series, one can obtain coil temperatures corresponding to the above specified conversion percentages and by simple subtraction obtain the "reduced temperature" at which the coil could be operated. This so-called "reduced temperature" is a function of input concentration so that it must be maximized for a given residual in order for the system to function properly regardless of input. Tables 10 and 11 maximize the reduced temperature for various residual outputs from 100 to 1000 ppm for both the experimental and extrapolated coil by using the subtraction method. Fig. 14 shows the necessary reduced temperature as a function of residual for both coils. The longer coil may be adequately operated at a temperature between 20° and 40°C cooler than the other, depending upon the allowable residual.

This method may be tested in the following manner:

1. Arbitrarily pick a residual concentration (100-1000 ppm) for either coil (6" or 12")

2. Find the corresponding $T_{reduced}$ on Fig. 14

3. Find the per cent conversion at $T_{reduced}$ on Fig. 10 (using the proper curve)

4. Arbitrarily select an input

5. Cross (3) with (4) in Fig. 13

6. By interpolation find the temperature increase caused by the reaction at this point

7. Add (6) to (2)

8. Find new per cent conversion corresponding to (7) on Fig. 10

9. Cross (8) with (4) on Fig. 13

10. If this first incremental temperature change has not placed you <u>above</u> the appropriate residual curve, repeat (6) through (9).

REFERENCES

1. R. L. Pullen and W. A. Sodeman, "Anoxia Resulting from Methane," 98, 5, November, 1945, 195-197.

2. W. J. Moore, Physical Chemistry, 2nd Edition, pp. 546-47 (1955).

Table 1

Internal Characteristics of Coil

	Corr./inch	Corr. Amplitude	Asbestos Thickness	No. of Layers	%Cross-Section Open	Ratio Vel.	Exposed area of Cat.(in^2)
(1)	9.5	40 mil	25 mil	9	64.5	1.83	160
(2)	15	34 mil	17 mil	11	56.7	1.76	210
(3)	20	21.5 mil	17 mil	15	47.7	2.10	280

Total cross-sectional area: 2.87 in^2

Area of core: 0.42 in^2

CH_4 Removal

Table 2

% Conversion

Flow, CFM	60 T_{air}	60 T_{coil}	70 T_{air}	70 T_{coil}	80 T_{air}	80 T_{coil}	90 T_{air}	90 T_{coil}
Pd at 1.2 mg/in^2 20 corr./in.								
0.11	-	442	310	450	340	465	375	500
0.22	323	443	338	455	360	484	400	530
0.33	-	-	364	440	380	462	416	512

Table 3

Pd at 6.0 mg/in^2 15 corr./in.								
0.11	403	450	408	460	422	480	450	526
0.22	-	-	380	430	410	465	470	540
0.33	-	-	396	445	424	480	470	550

Table 4

Pd at 1.2 mg/in^2 15 corr./in.								
0.11	350	468	360	487	380	517	415	568
0.22	425	470	433	484	448	504	480	550
0.33	420	467	440	488	468	522	522	595

Table 5

Pd at 1.2 mg/in^2 9.5 corr./in.								
0.11	406	524	416	540	430	566	447	610
0.22	420	546	436	567	466	600	-	-
0.33	456	564	470	588	488	612	-	-

CO Removal

Table 6

Flow, CFM	% Conversion 60 T_{air}	60 T_{coil}	70 T_{air}	70 T_{coil}	80 T_{air}	80 T_{coil}	90 T_{air}	90 T_{coil}
Pd at 1.2 mg/in^2 15 corr./in.								
0.11	159	195	161	198	164	206	172	224
0.22	187	203	191	212	200	224	216	244
0.33	182	214	188	218	200	225	222	246

Table 7

Pd at 1.2 mg/in^2 0.5 corr./in.								
0.11	170	204	173	210	177	220	185	234
0.22	212	252	219	260	230	272	250	292
0.33	-	-	228	260	246	276	274	306

Table 8

Per Cent Removal vs Catalyst Length

% Removal by 1 unit	by 2 units	by 3 units	by 4 units
30	51	66	76
40	64	78	87
50	75	87.5	94
60	84	94	98
70	91	97	99
80	96	99	-

Table 9

Efficiency of Unit (at 9.5 corr./inch) Without Precious Metal Catalyst

Gas	Flow (CFM)	T_{air}	T_{coil}	% Removal
CO	0.22	245	*	20
CO	0.22	365	*	67
CO	0.22	440	*	88
H_2 (5000 ppm)**	0.22	440	460	70
H_2 (5000 ppm)**	0.22	470	508	80
H_2 (5000 ppm)**	0.22	560	626	96
CH_4	0.22	570	624	29

* No thermocouples welded to metal during this series.

**Concentration of H_2 is recorded since it is not a first order reaction, so that the extent of oxidation depends on concentration.

Table 10

Determination of $T_{reduced}$ vs. Residual Methane for 6" Unit

	% Conversion	$T_{conversion}$ (°C)	$\Delta T_{enthalpy}$ (°C)	$T_{reduced}$ (°C)
100 ppm Residual	75.7	372	10	362
	82.0	383	15	368
	86.0	391	20	371
	88.5	397	25	372*
	90.2	400	30	370
	92.2	406	40	366
300 ppm Residual	60.0	351	15	336
	66.8	359	20	339
	71.4	365	25	340
	75.2	371	30	341*
	80.3	379	40	339
	83.6	386	50	336
500 ppm Residual	47.6	339	15	324
	54.8	345	20	325
	60.4	351	25	326*
	64.8	355	30	325
	71.5	365	40	328
	76.0	372	50	322
1000 ppm Residual	31.8	323	15	308
	38.0	330	20	310
	43.0	335	25	310*
	47.8	339	30	309
	55.0	346	40	306
	60.3	351	50	299

*Indicated Maximum $T_{reduced}$

Table 11

Determination of $T_{reduced}$ vs. Residual Methane for 12" Unit

	% Conversion	$T_{conversion}$ (°C)	$\Delta T_{enthalpy}$ (°C)	$T_{reduced}$ (°C)
100 ppm Residual	75.7	341	10	331
	82.0	349	15	334
	86.0	354	20	334*
	88.5	358	25	333
	90.2	361	30	331
	92.2	365	40	325
300 ppm Residual	60.0	329	15	314
	66.8	334	20	314
	71.4	340	25	315*
	75.2	343	30	313
	80.3	346	40	306
	83.6	358	50	308
500 ppm Residual	47.6	320	15	305
	54.8	326	20	306*
	60.4	329	25	304
	64.8	332	30	302
	71.5	338	40	298
	76.0	341	50	291
1000 ppm Residual	31.8	-	15	-
	38.0	-	20	-
	43.0	318	25	293*
	47.8	321	30	291
	55.0	326	40	286
	60.3	329	50	279

* Indicated maximum $T_{reduced}$

Table 12

Breakdown of Weight for Proposed Air Purification System

1.	Catalyst - including heater, core and container	2.1 lbs.
2.	Insulation - (Min-k 1301)	2.87 lbs.
3.	Heat loss through insulation	6.64 lbs.
4.	Heat exchanger weight	4.20 lbs.
5.	Heat loss through exchanger	4.4 lbs.
6.	Pressure drop through system (2" H_2O)	0.35 lbs.
7.	Frame (20 gage stainless steel)	4.12 lbs.
	Total Weight	24.68 lbs.

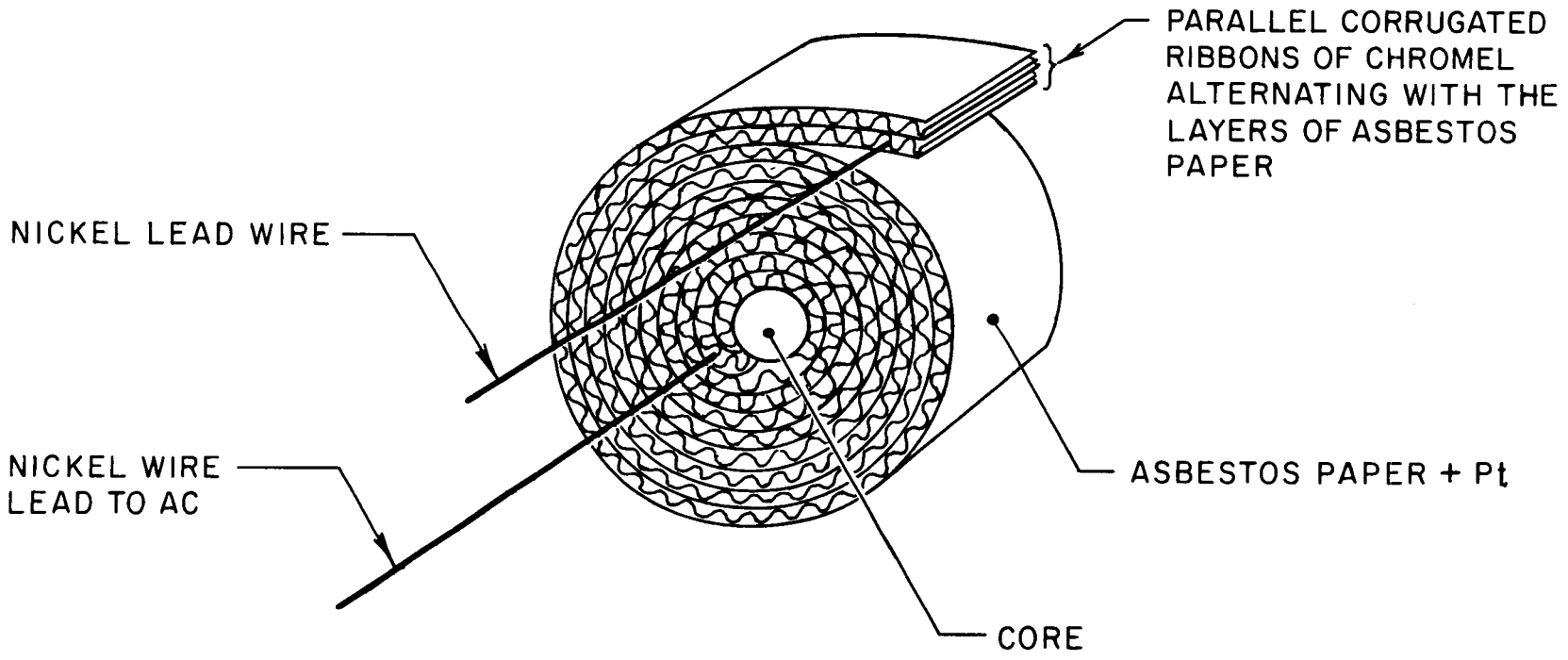


FIG.1 CATALYTIC COMBUSTION UNIT

(Patent Pending)

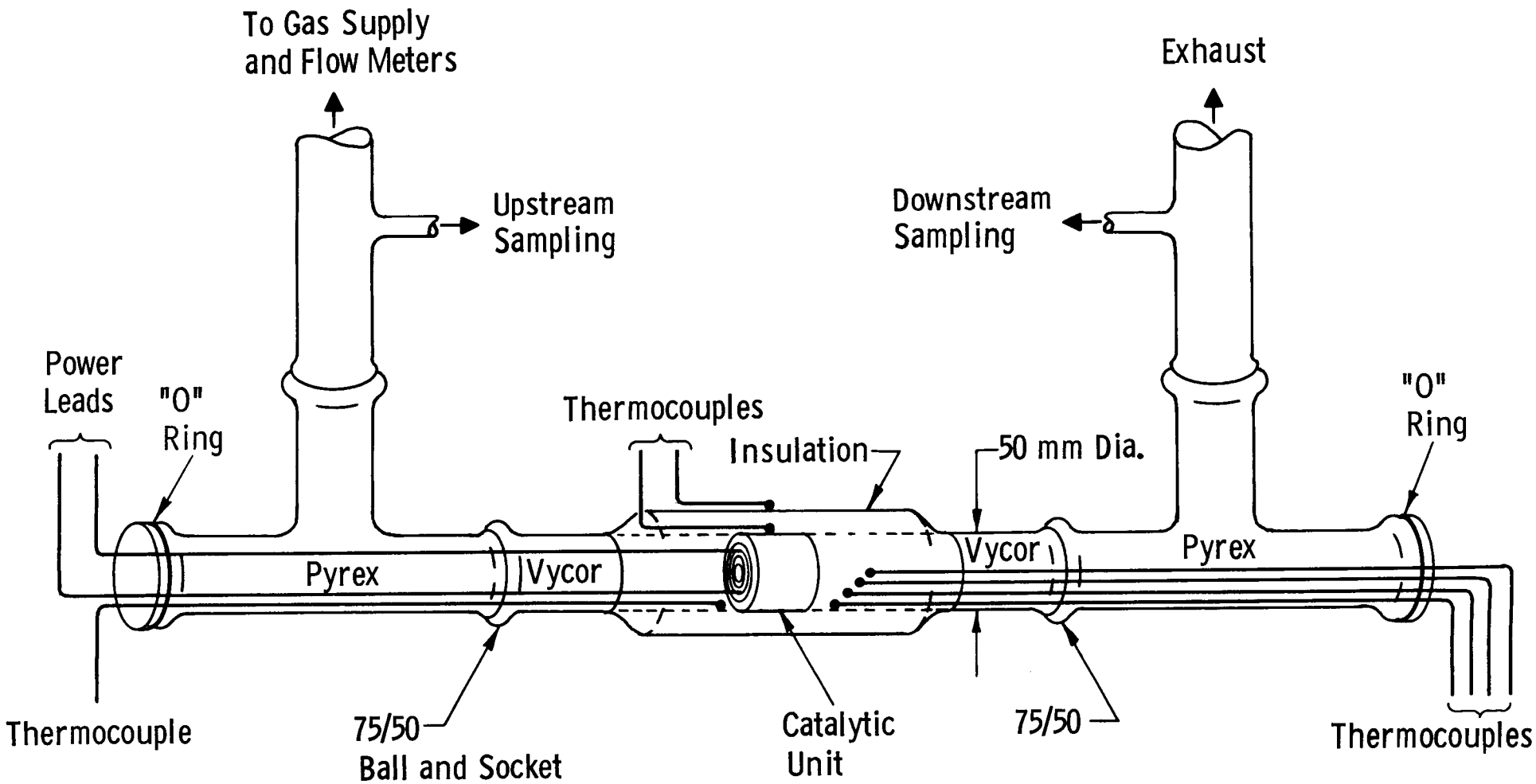


FIG.2 CATALYTIC REACTION TUBE

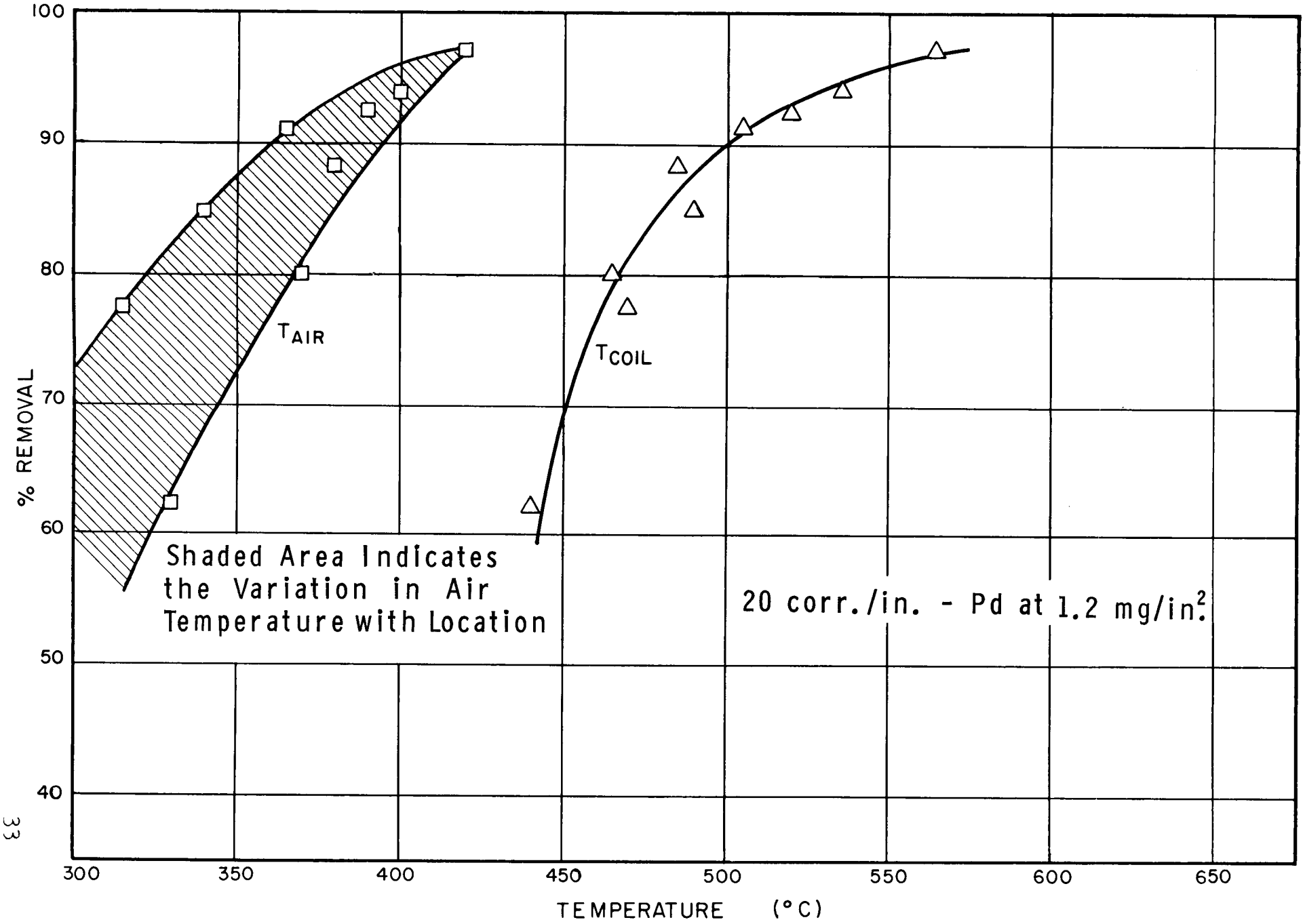


FIG.3A CH_4 REMOVAL AT 0.11 CFM

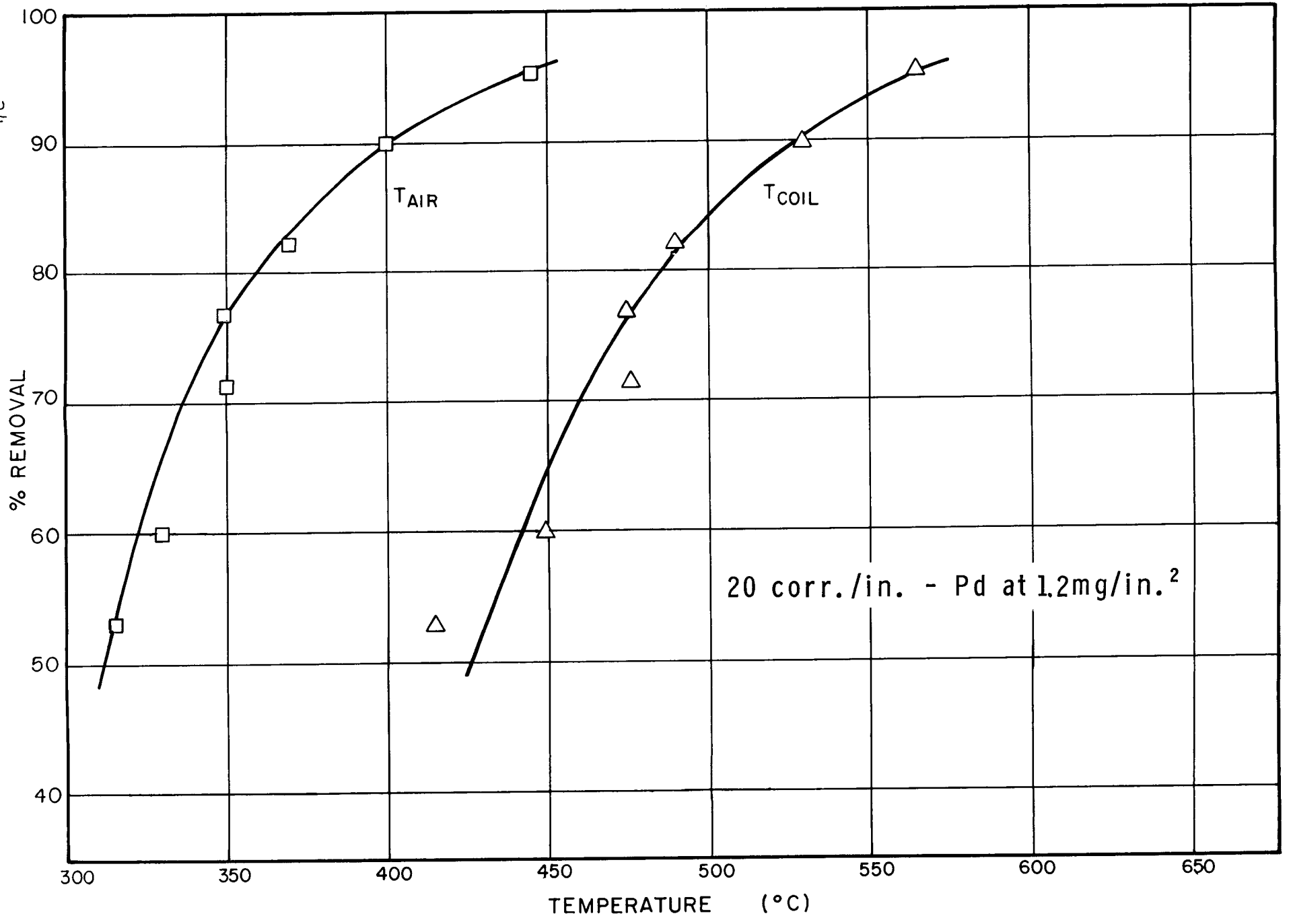


FIG. 3B CH_4 REMOVAL AT 0.22 CFM

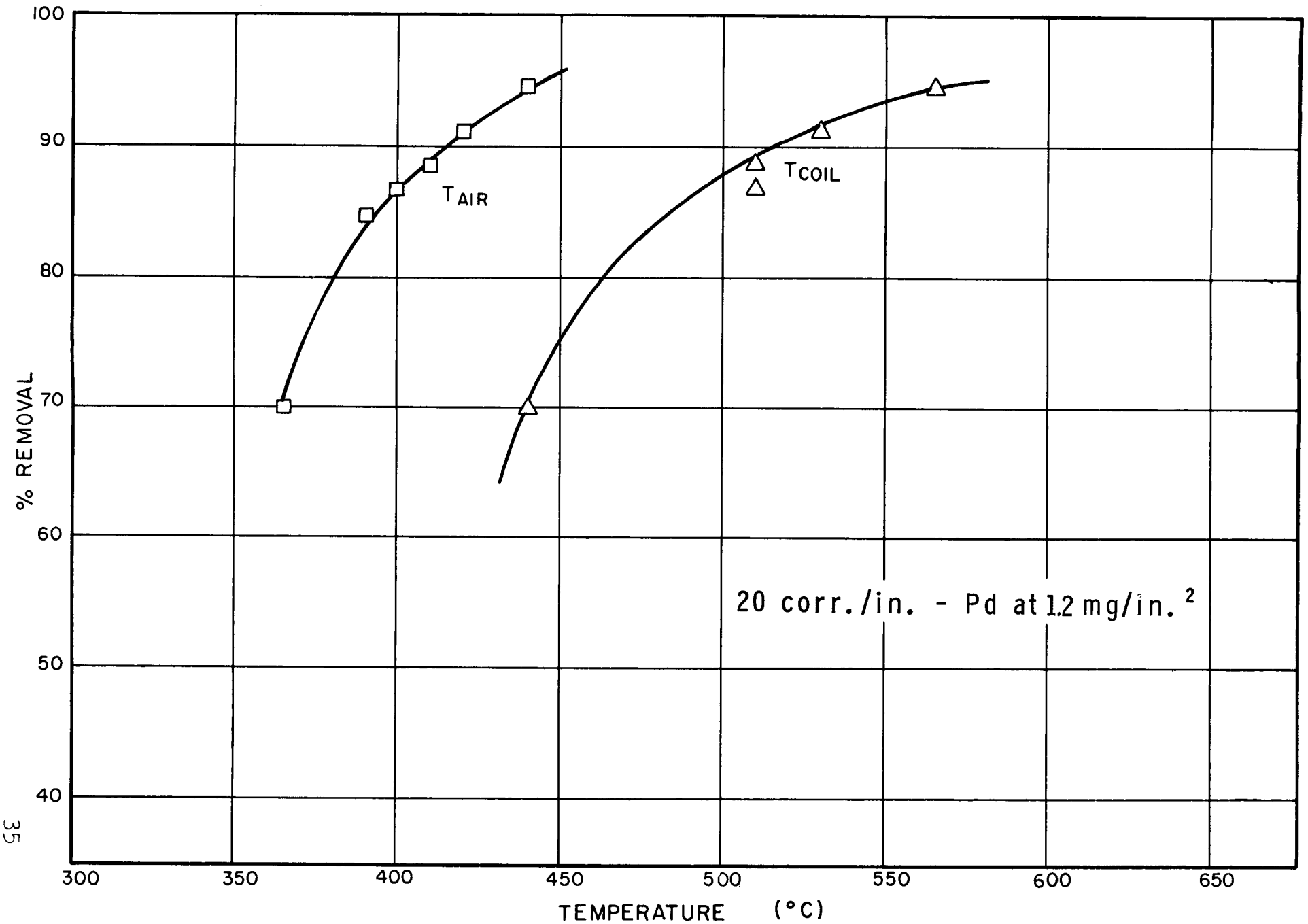


FIG.3C CH_4 REMOVAL AT 0.33 CFM

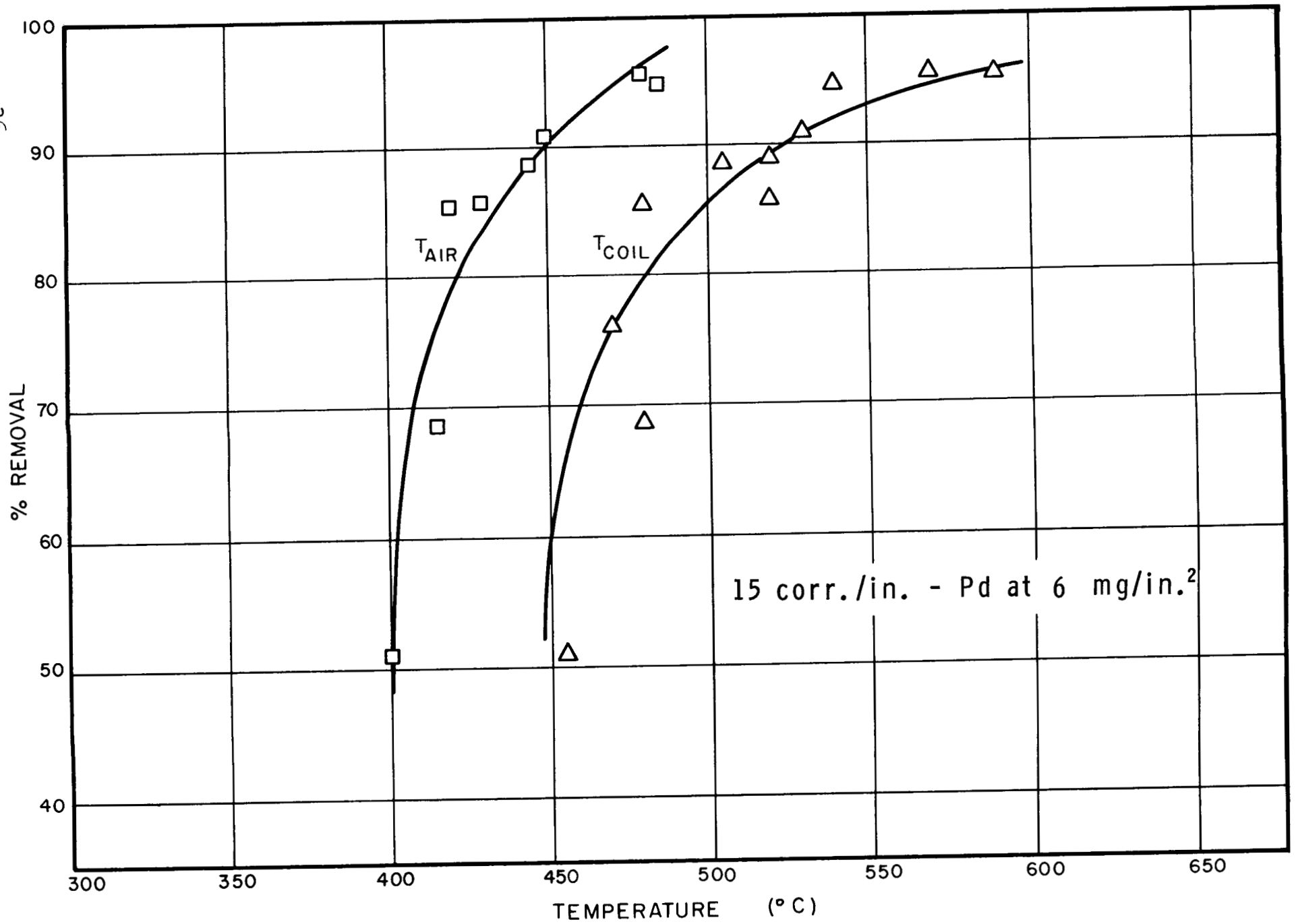


FIG. 4A CH_4 REMOVAL AT 0.11 CFM

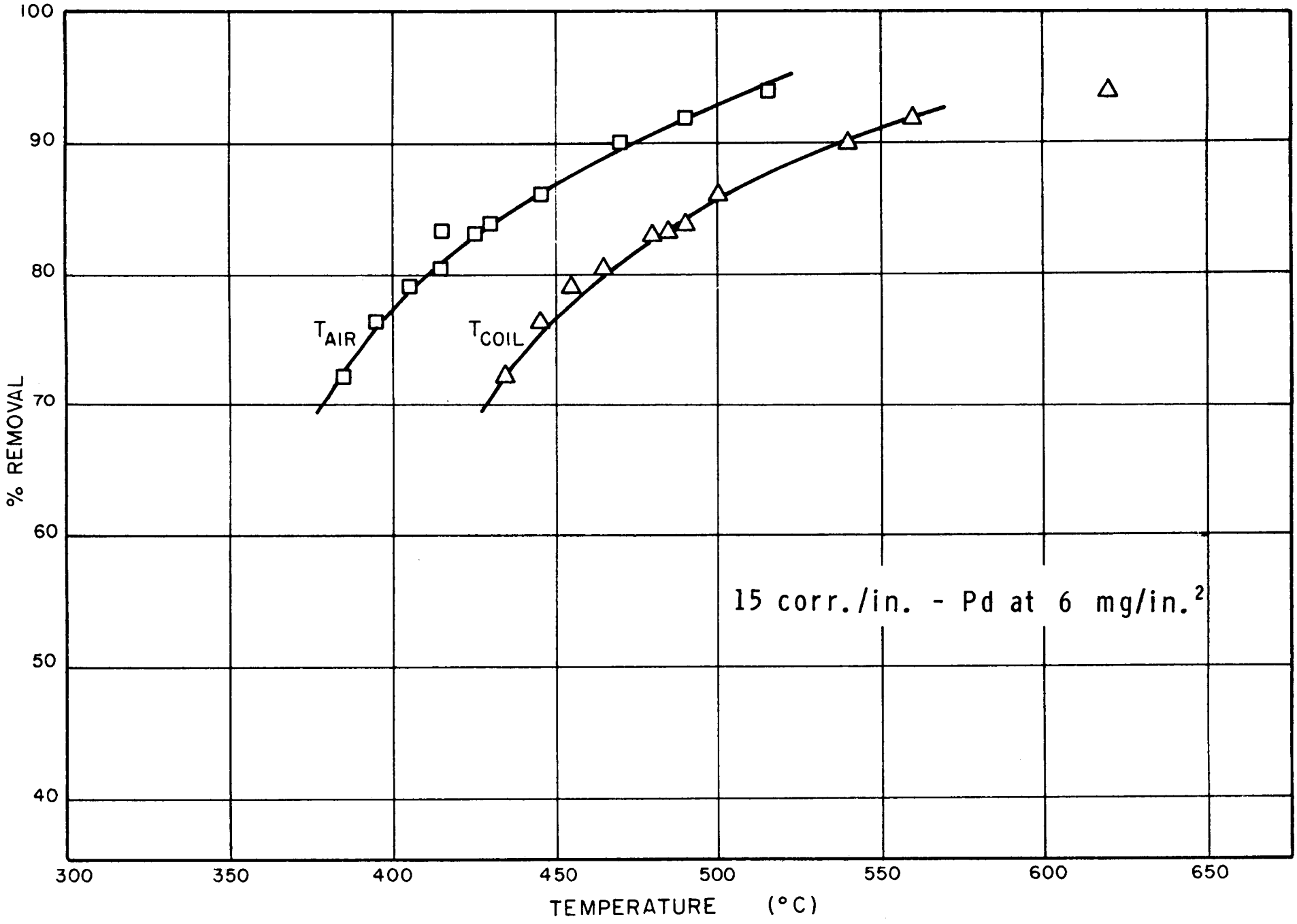


FIG. 4B CH_4 REMOVAL AT 0.22 CFM

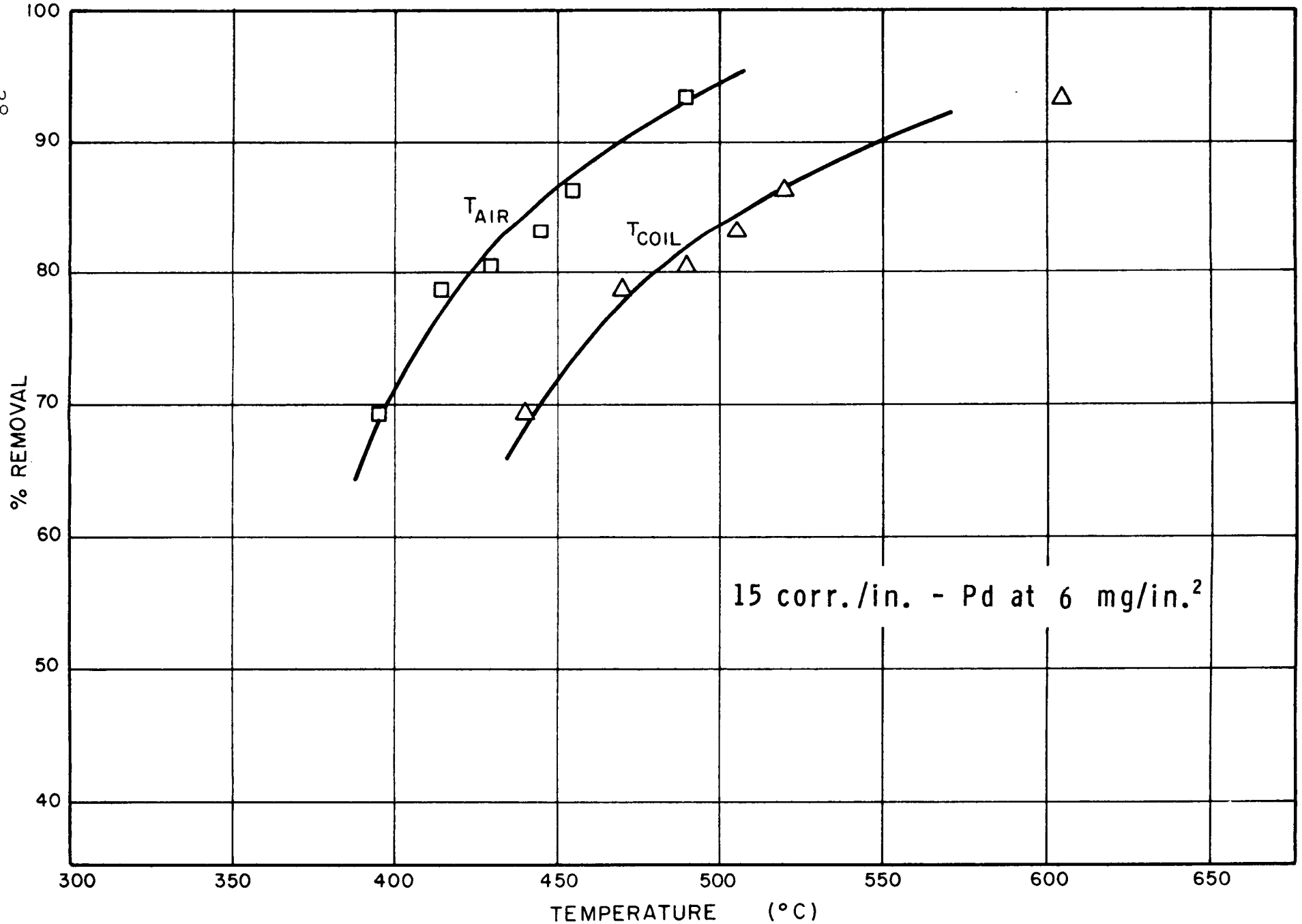


FIG. 4C CH_4 REMOVAL AT 0.33 CFM

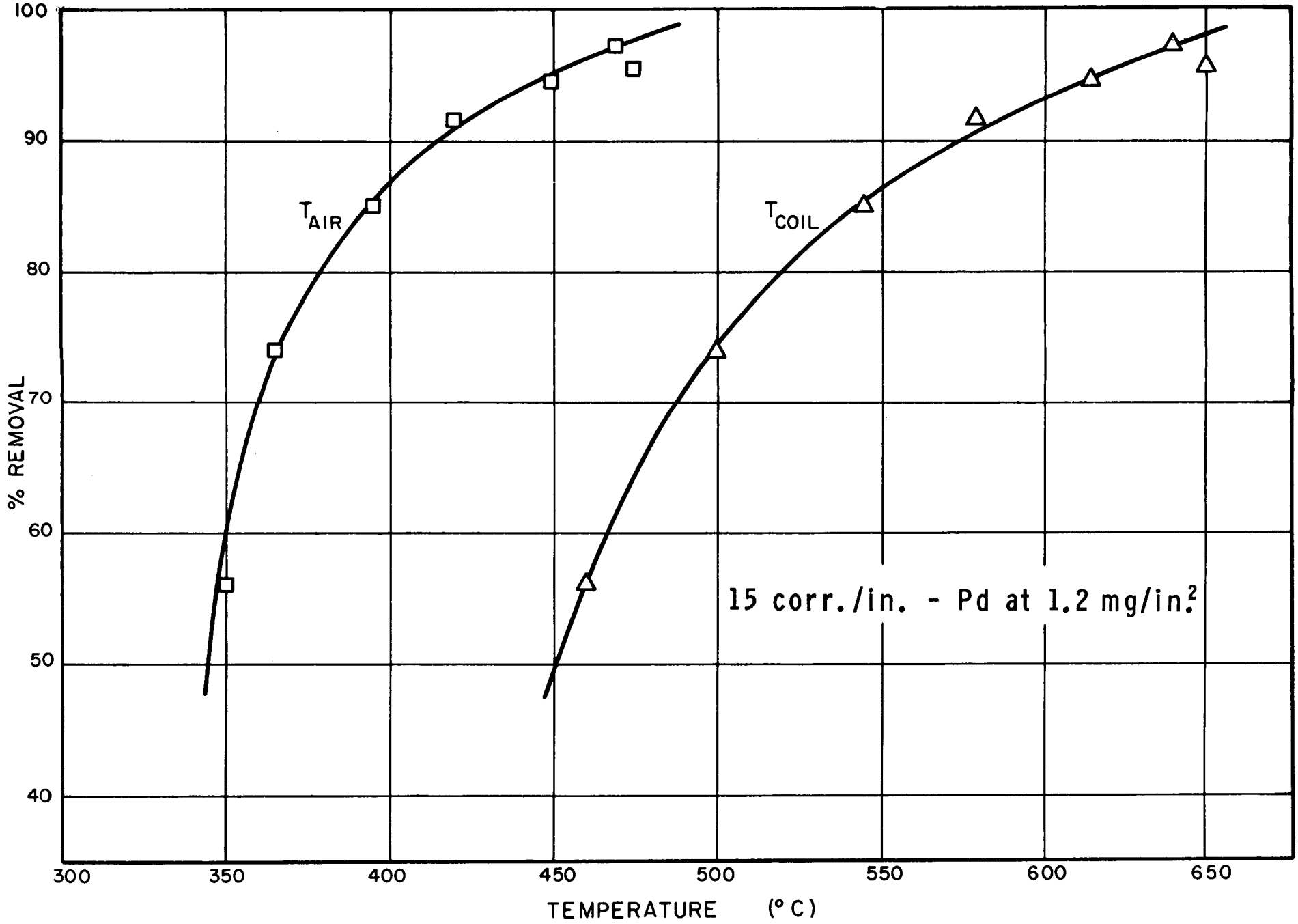


FIG. 5A CH_4 REMOVAL AT 0.11 CFM

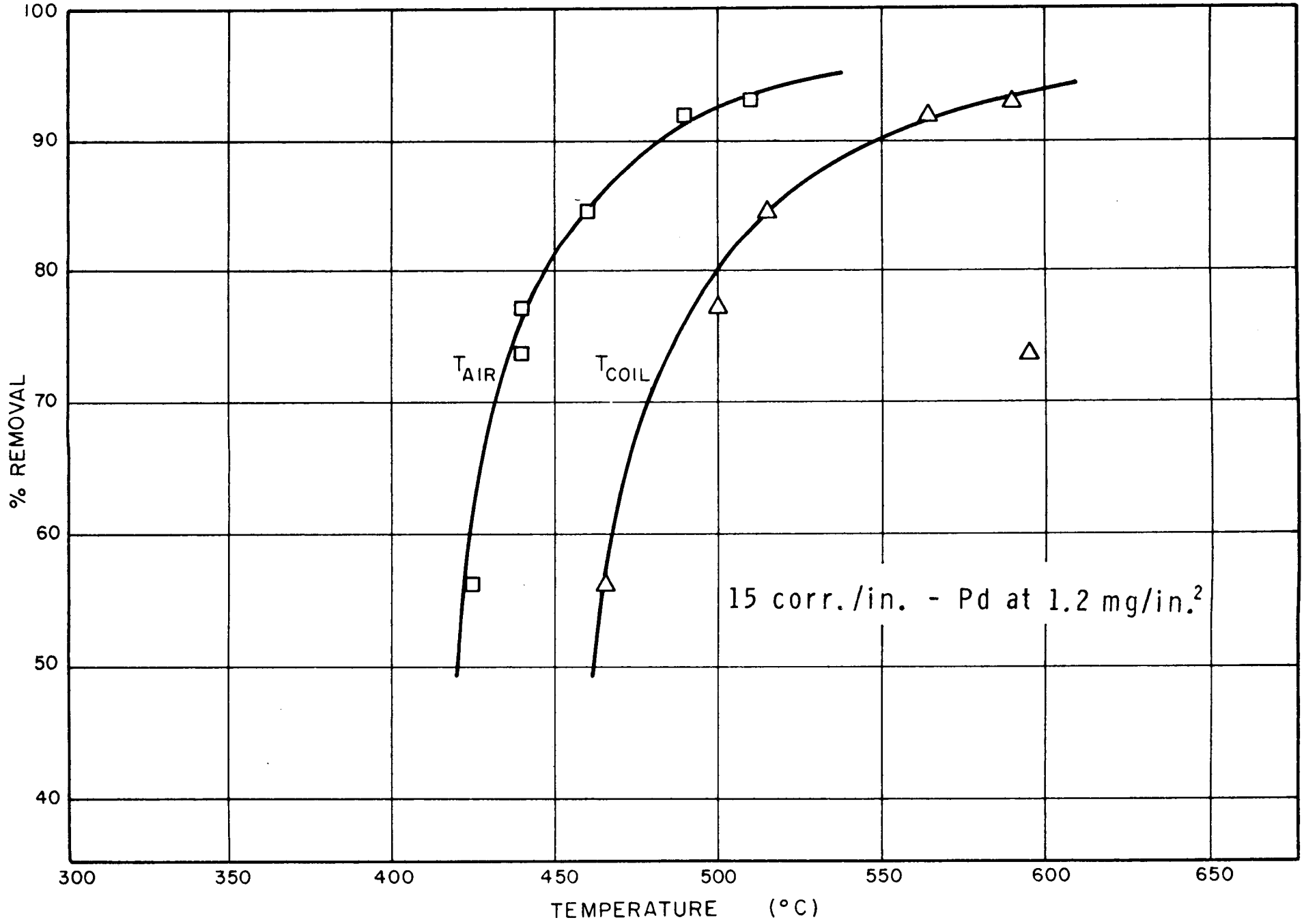


FIG. 5B CH_4 REMOVAL AT 0.22 CFM

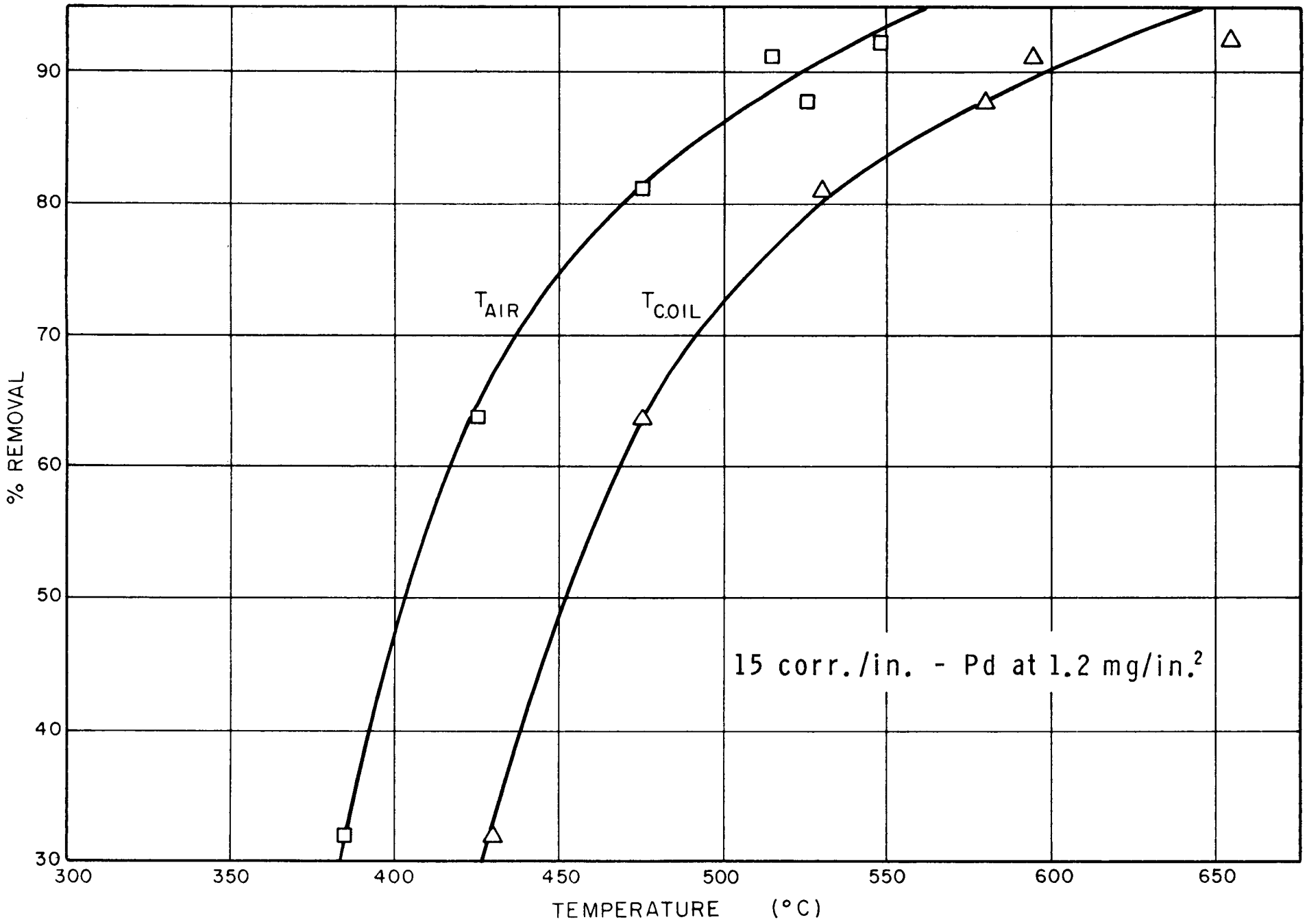


FIG. 5C CH_4 REMOVAL AT 0.33 CFM

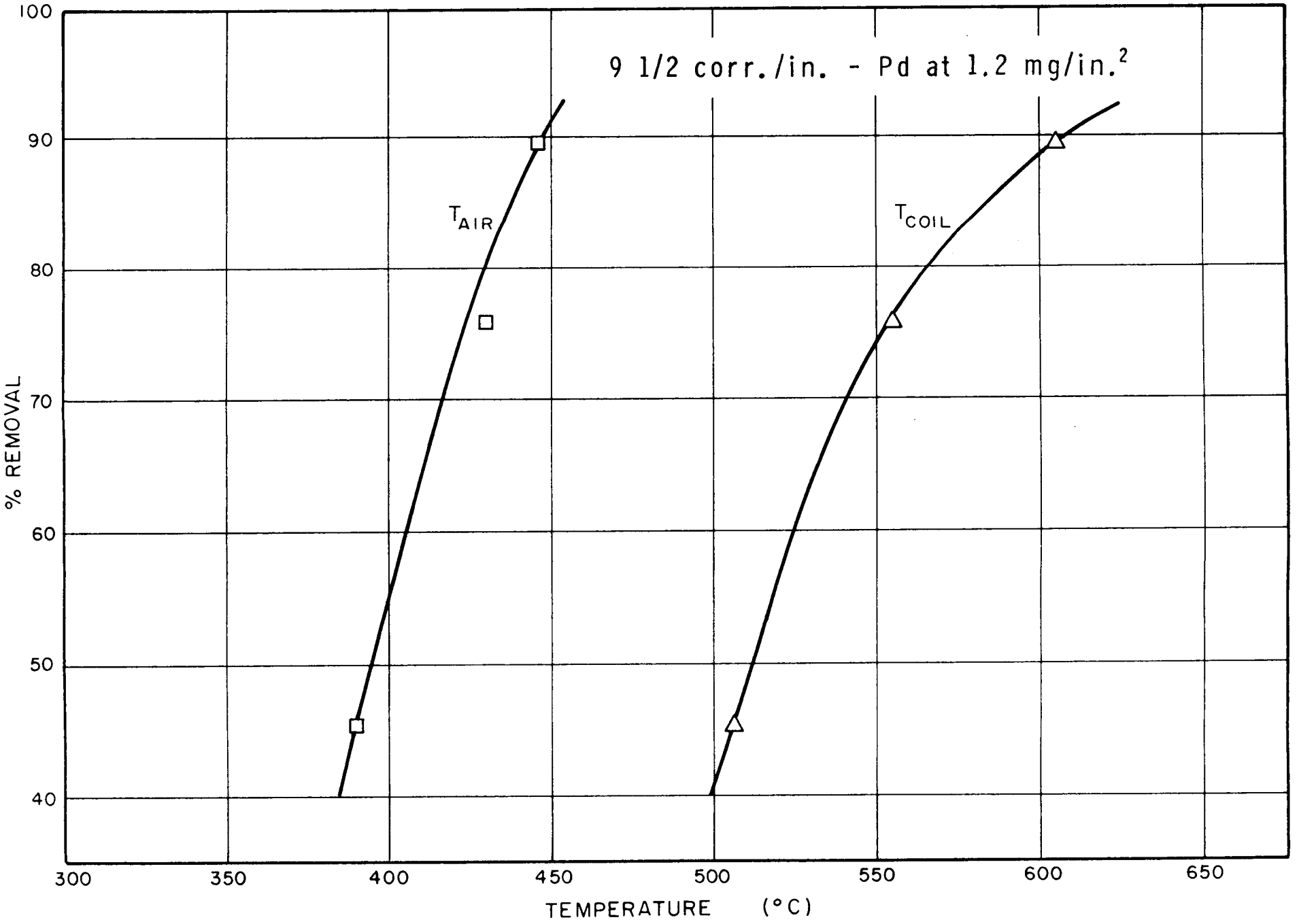


FIG. 6A CH_4 REMOVAL AT 0.11 CFM

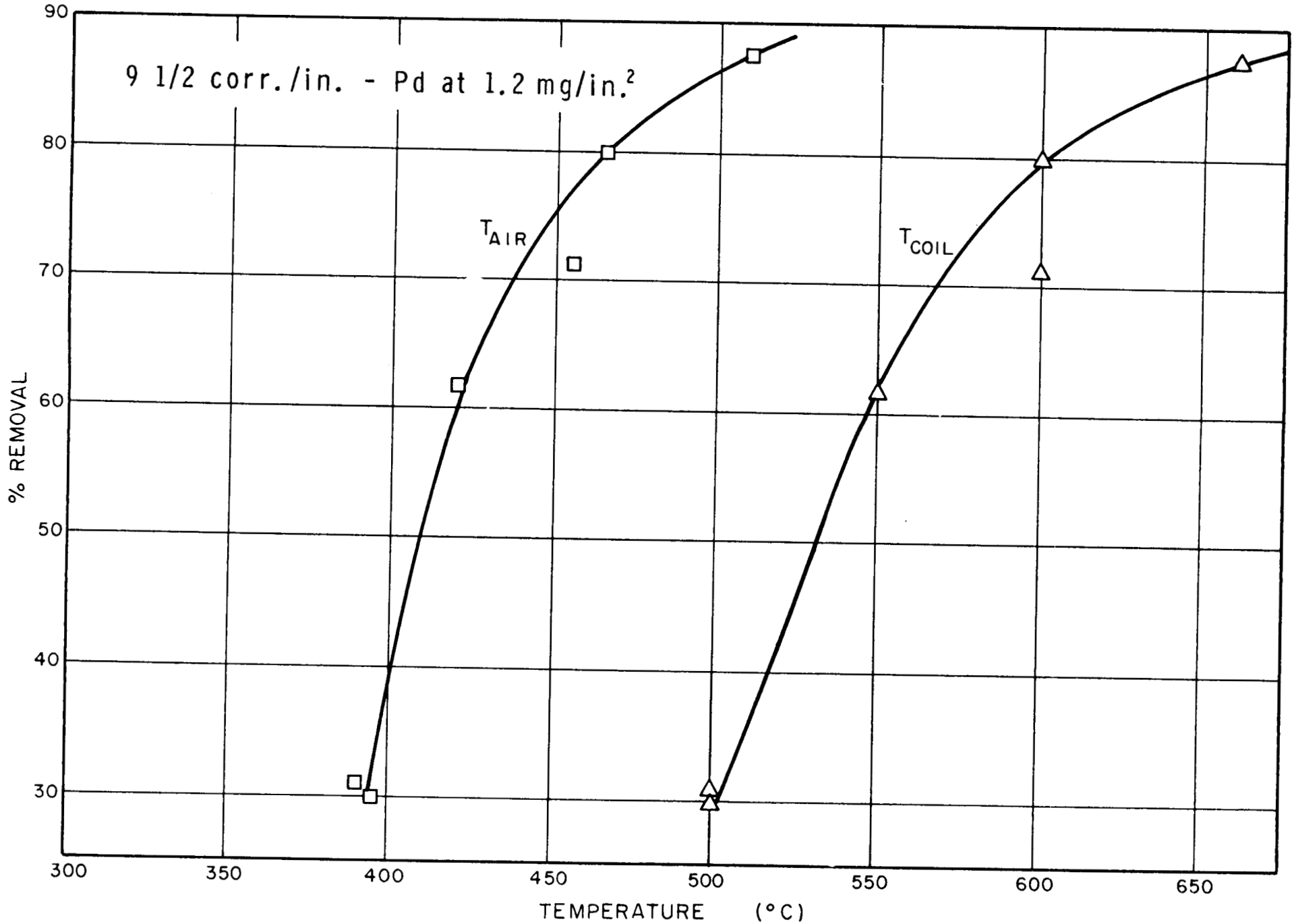


FIG. 6B CH_4 REMOVAL AT 0.22 CFM

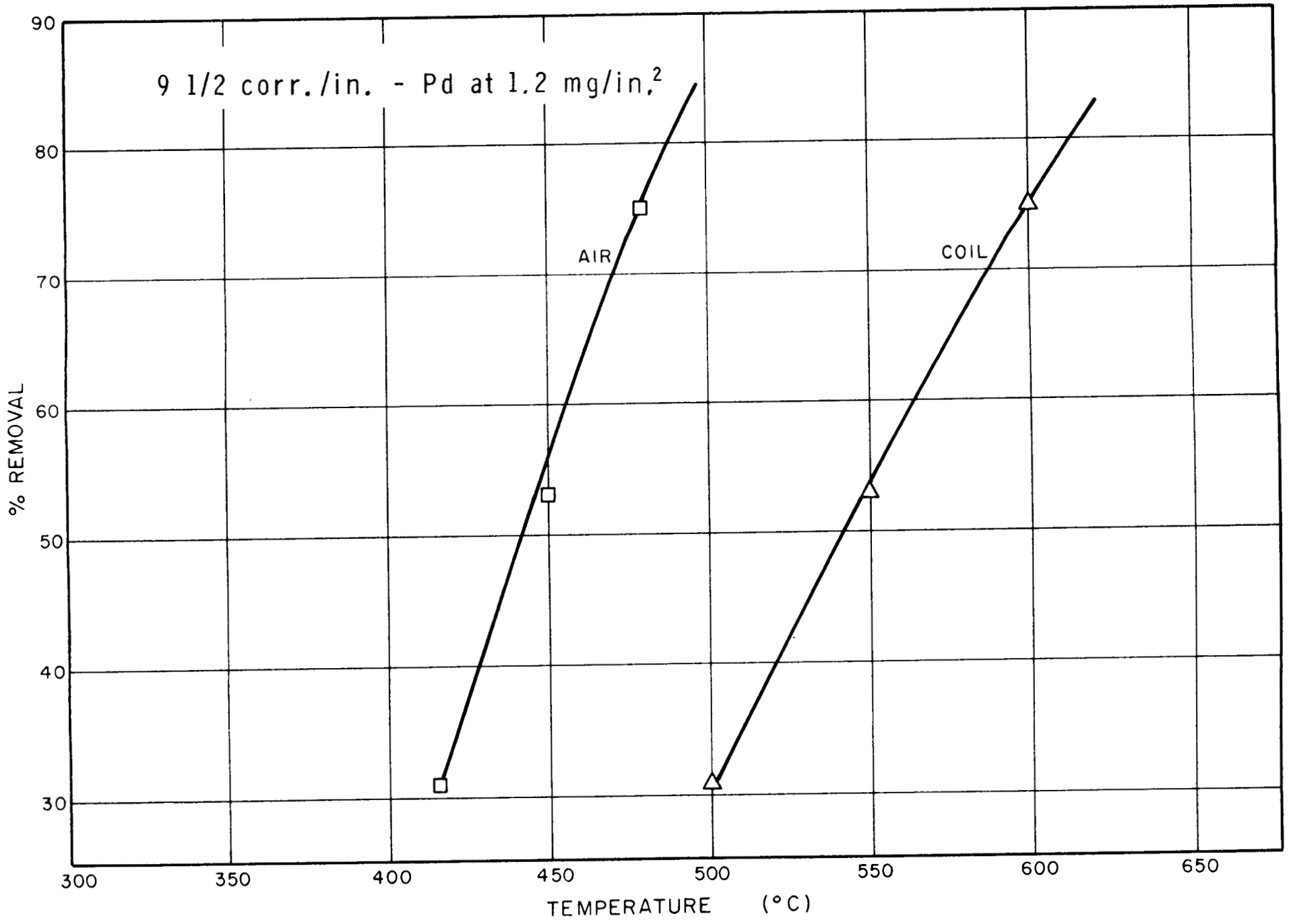


FIG. 6C CH_4 REMOVAL AT 0.33 CFM

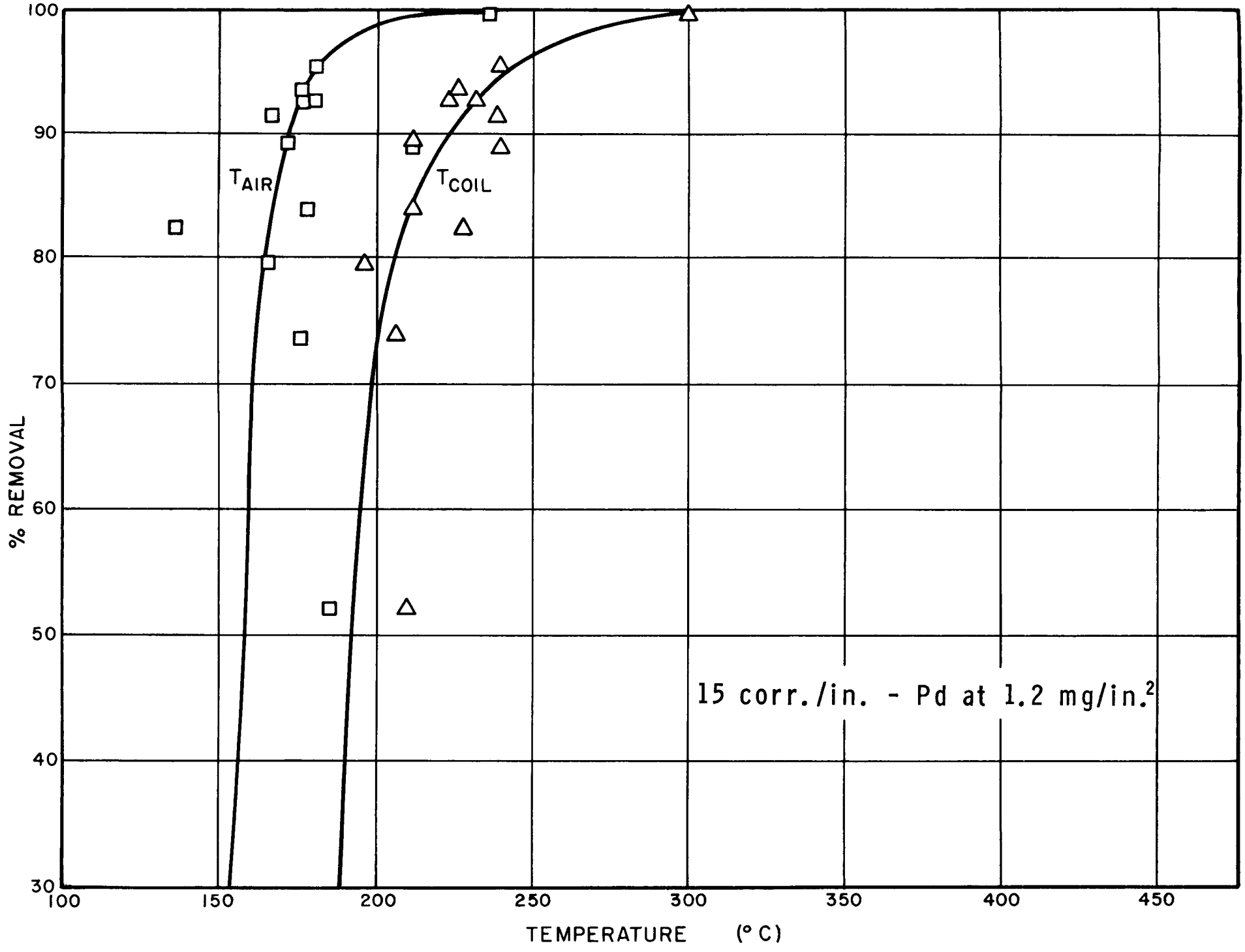


FIG. 7A CO REMOVAL AT 0.11 CFM

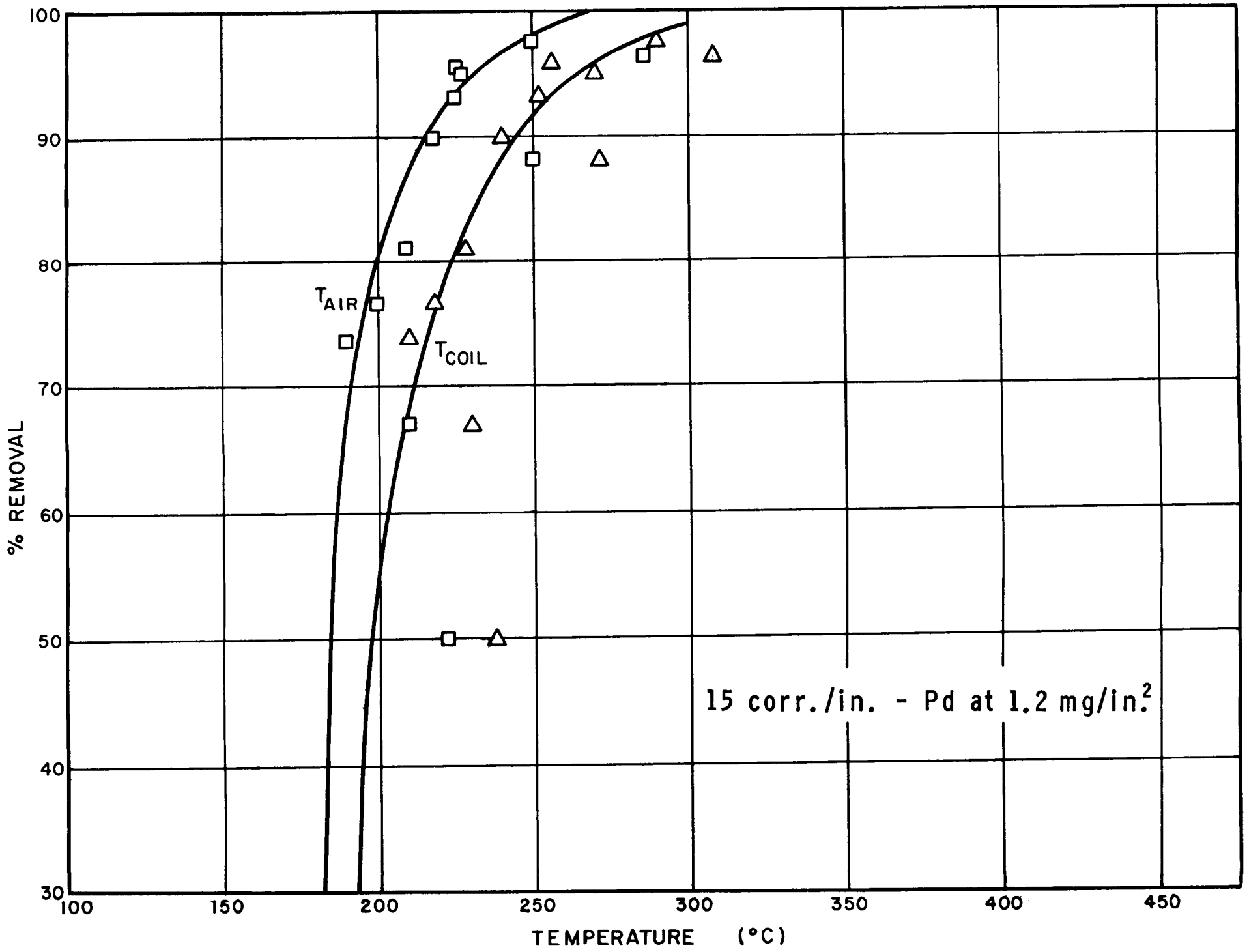


FIG. 7B CO REMOVAL AT 0.22 CFM

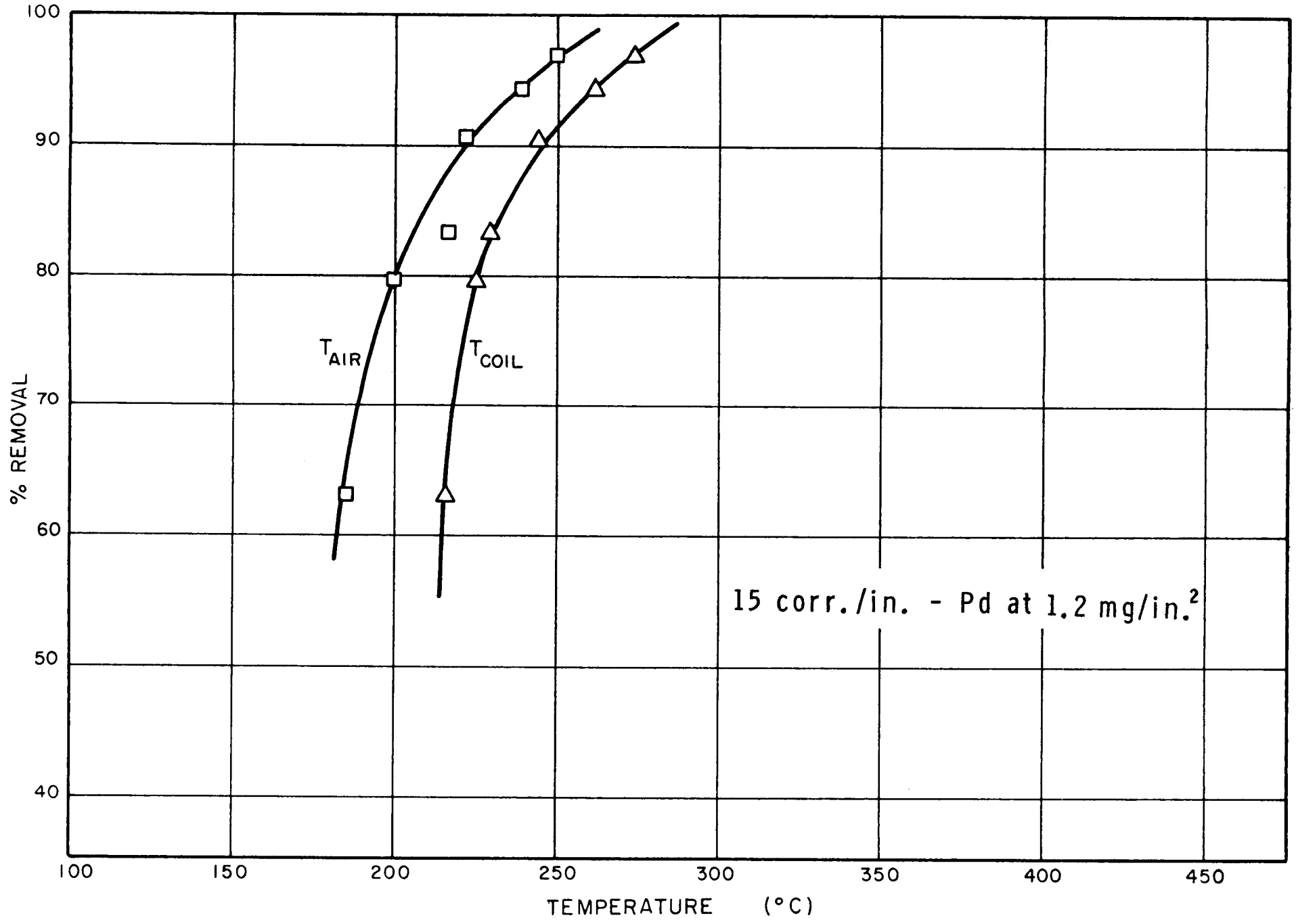


FIG. 7C CO REMOVAL AT 0.33 CFM

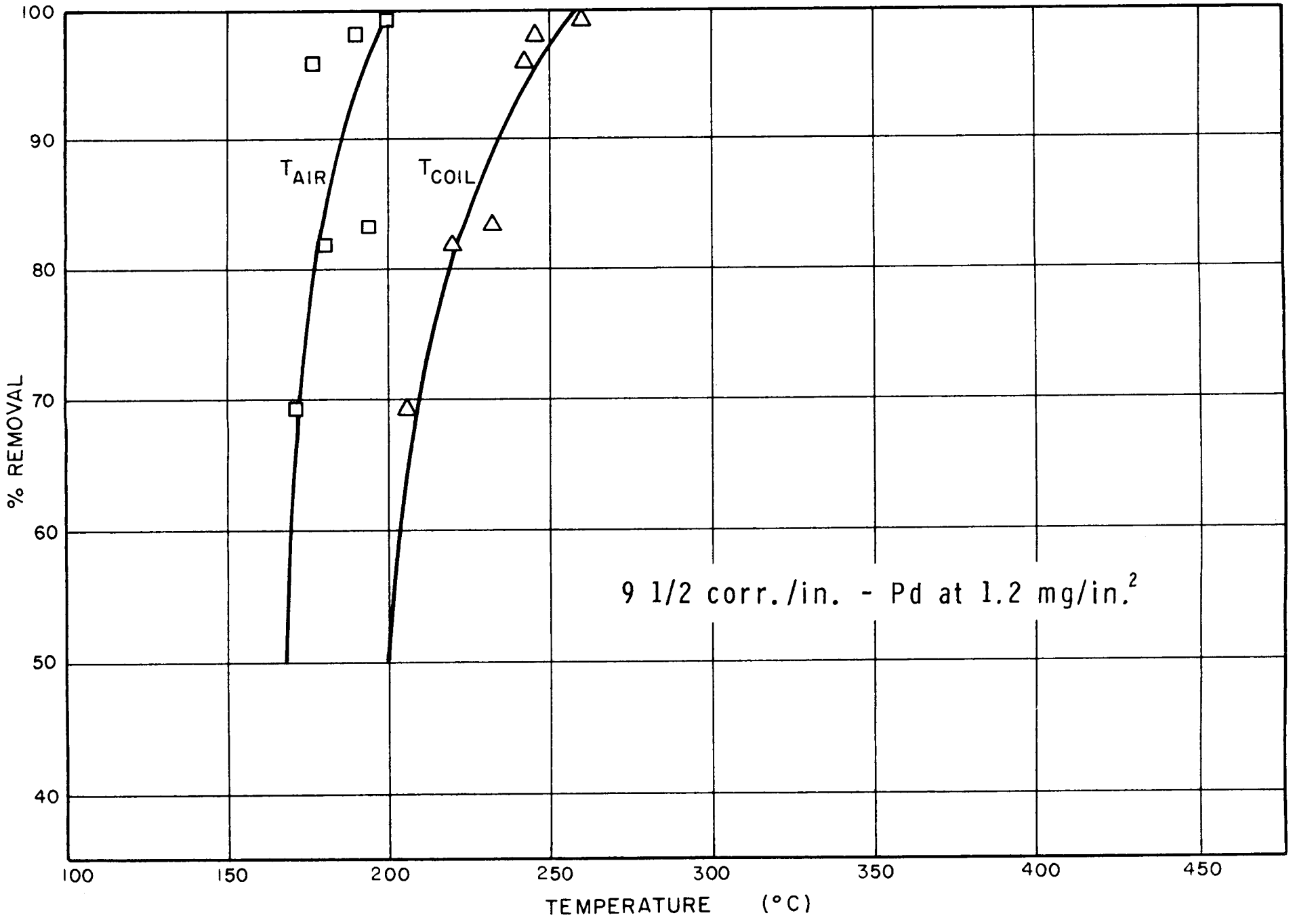


FIG. 8A CO REMOVAL AT 0.11 CFM

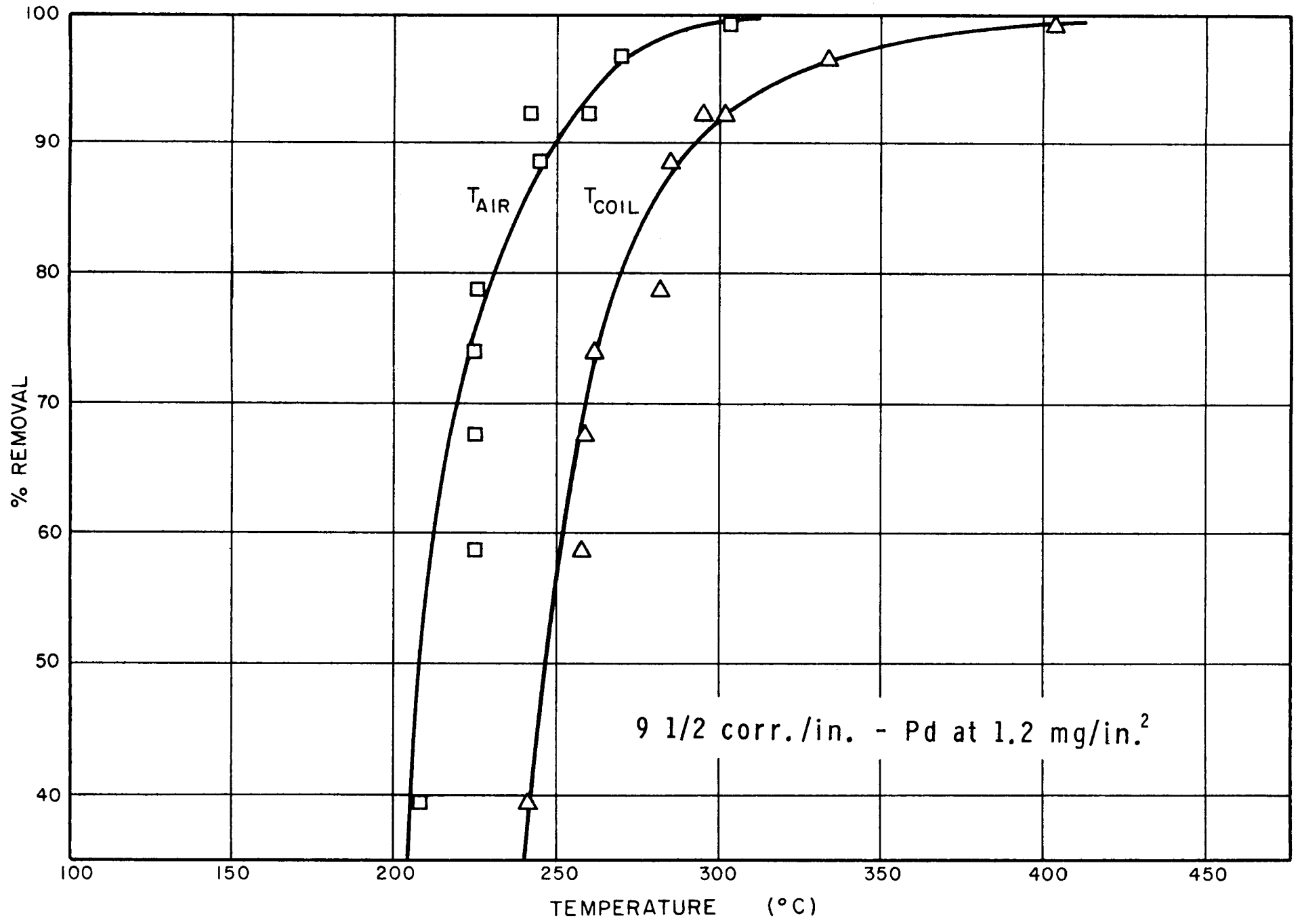


FIG.8B CO REMOVAL AT 0.22 CFM

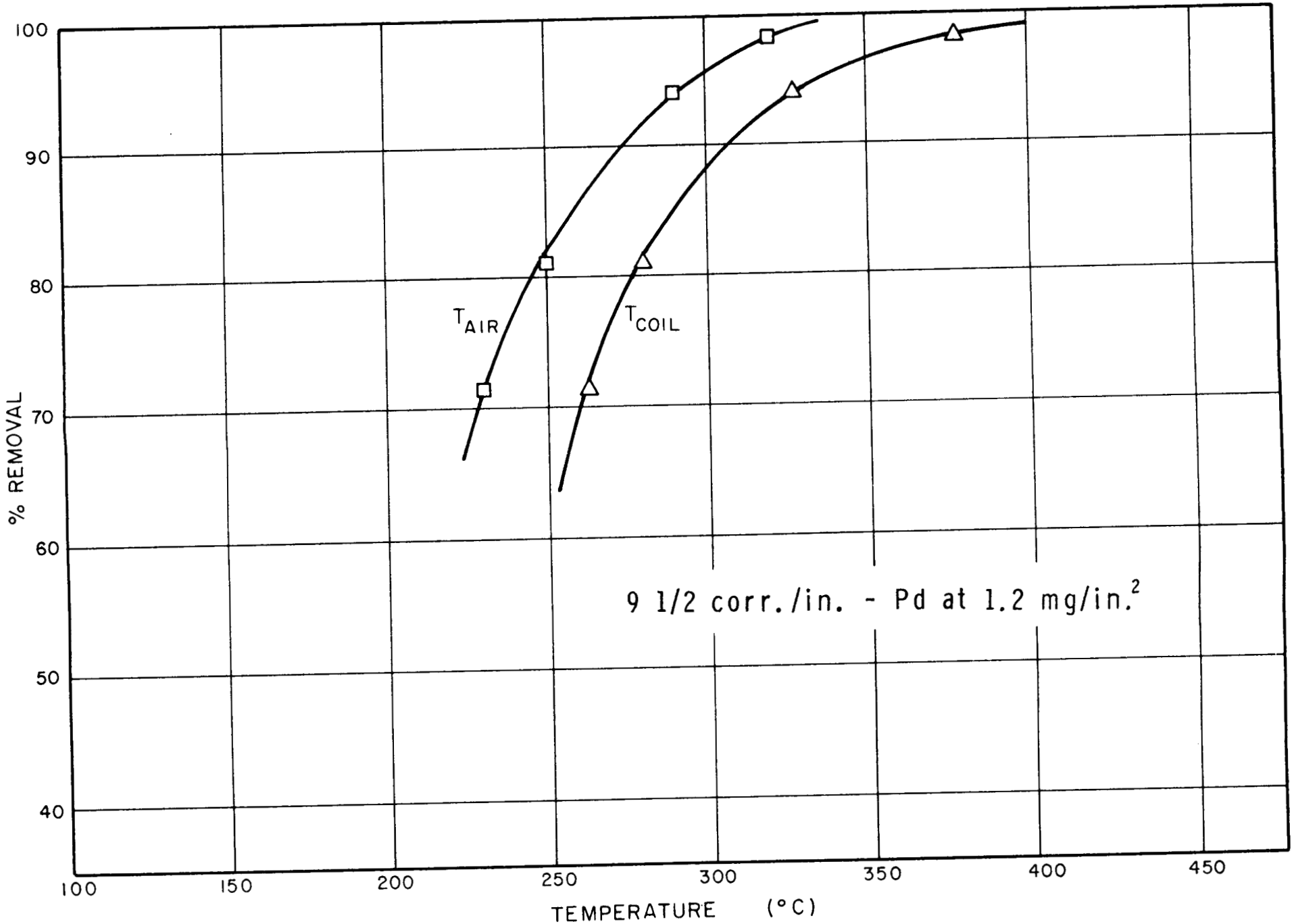


FIG. 8C CO REMOVAL AT 0.33 CFM

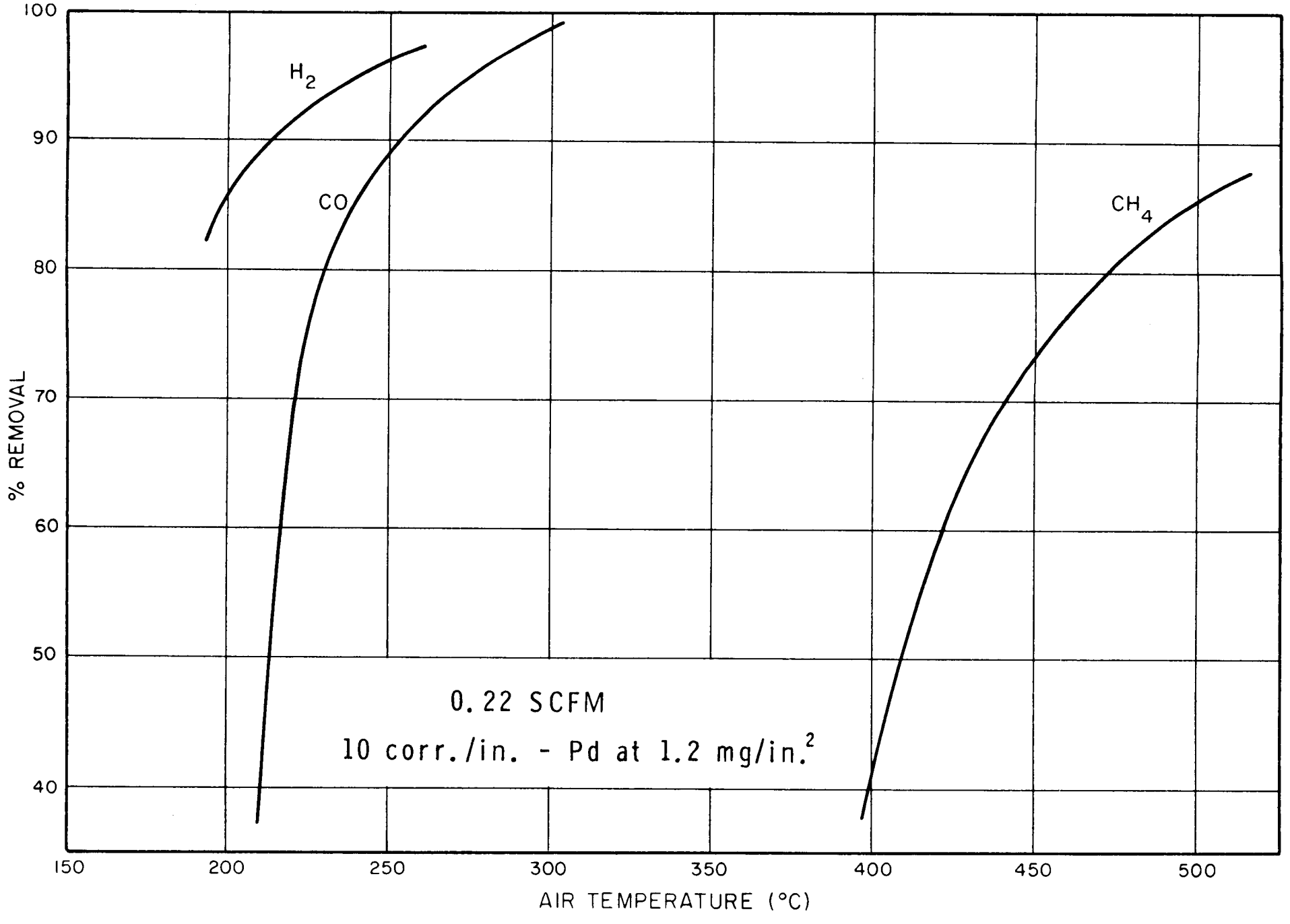


FIG. 9 ENERGY COMPARISON FOR OXIDATION OF GASES

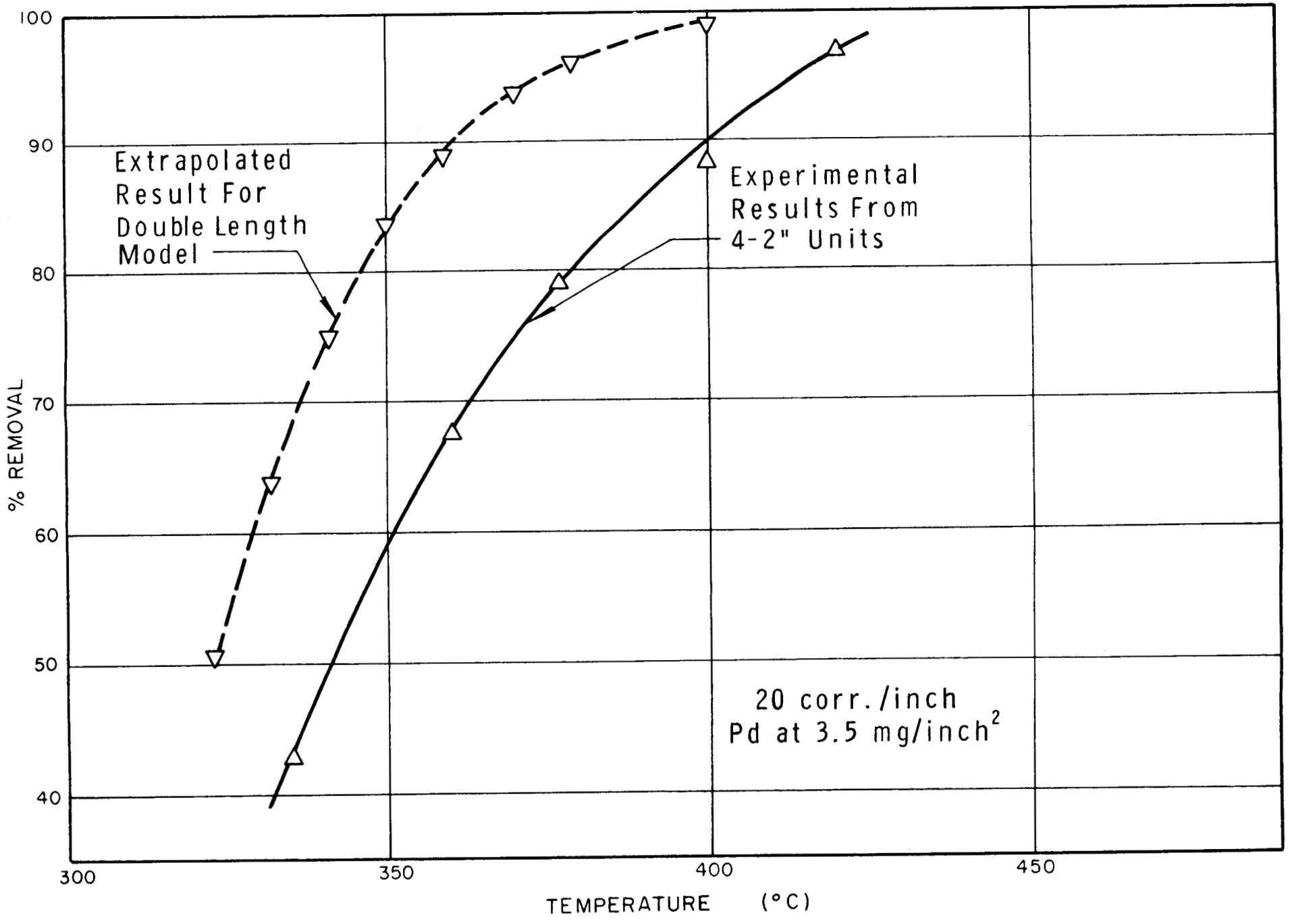


FIG. 10 METHANE REMOVAL AT 0.40 CFM

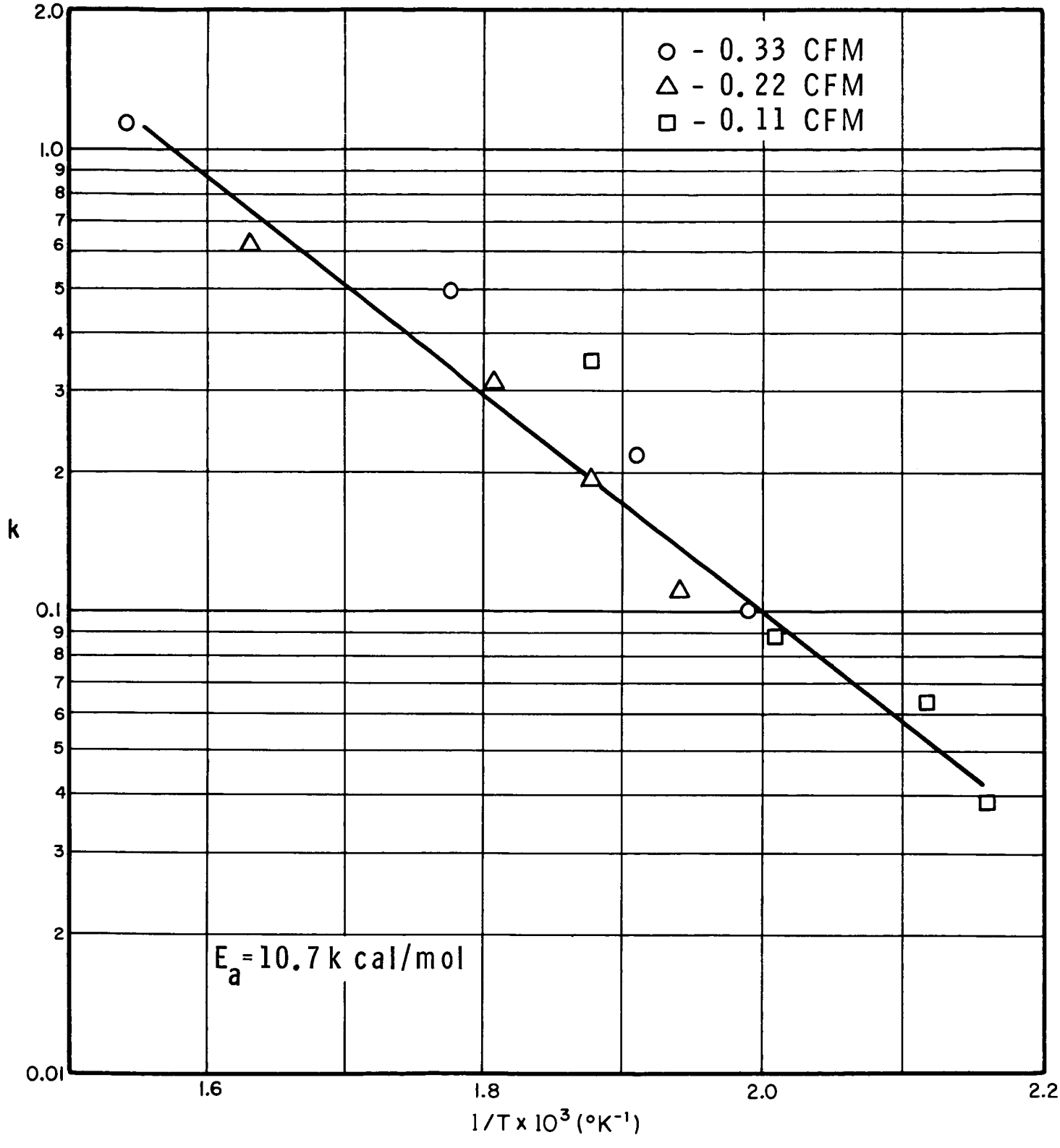


FIG. 11 DETERMINATION OF ACTIVATION ENERGY OF CO IN SYTEM WITH Pd AT 1.2 MG/IN² + 9.5 CORR/INCH

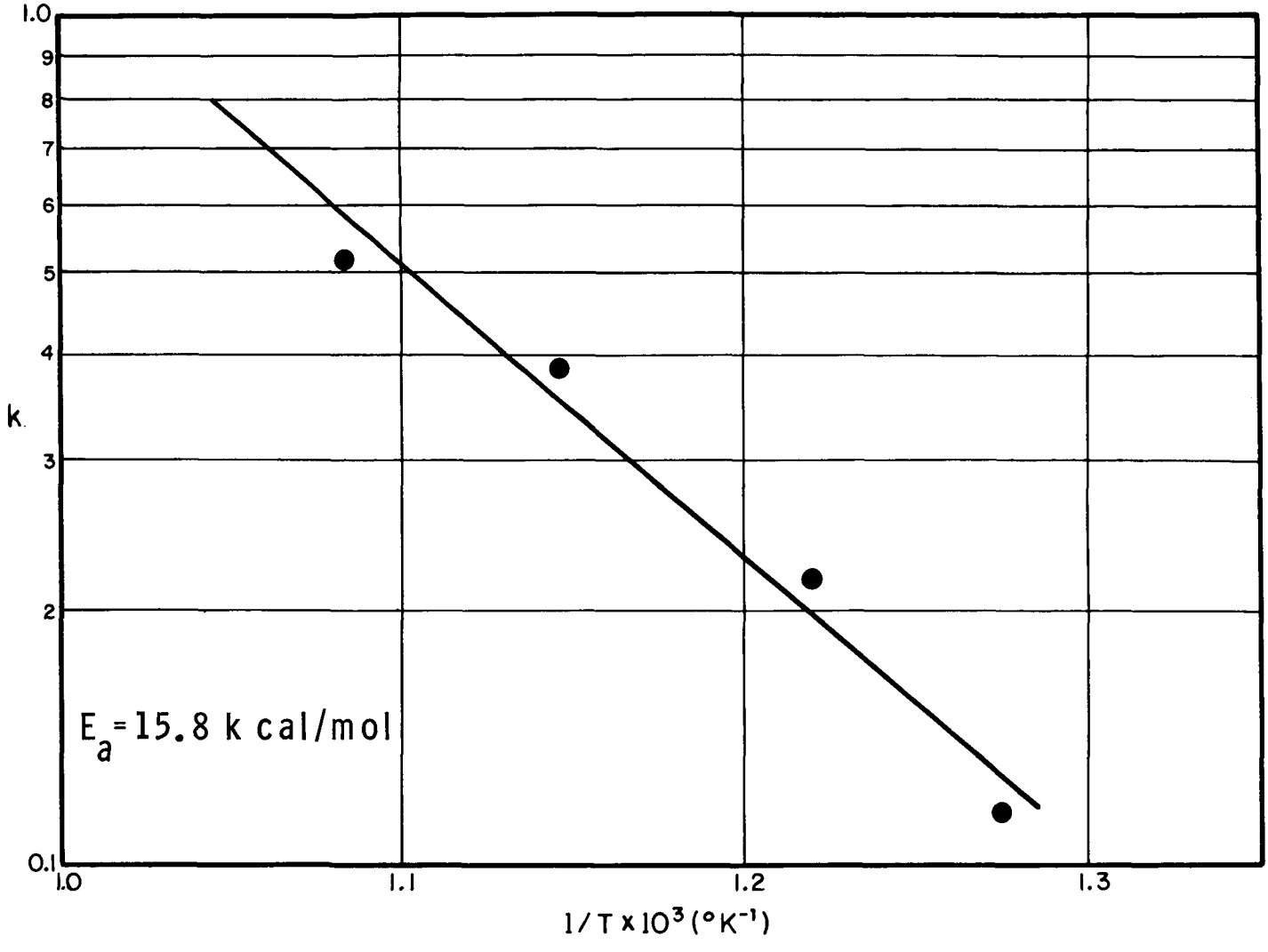


FIG. 12 DETERMINATION OF ACTIVATION ENERGY OF CH_4 IN SYSTEM WITH Pd AT 1.2 MG/IN.^{2} + 9.5 CORR/IN.

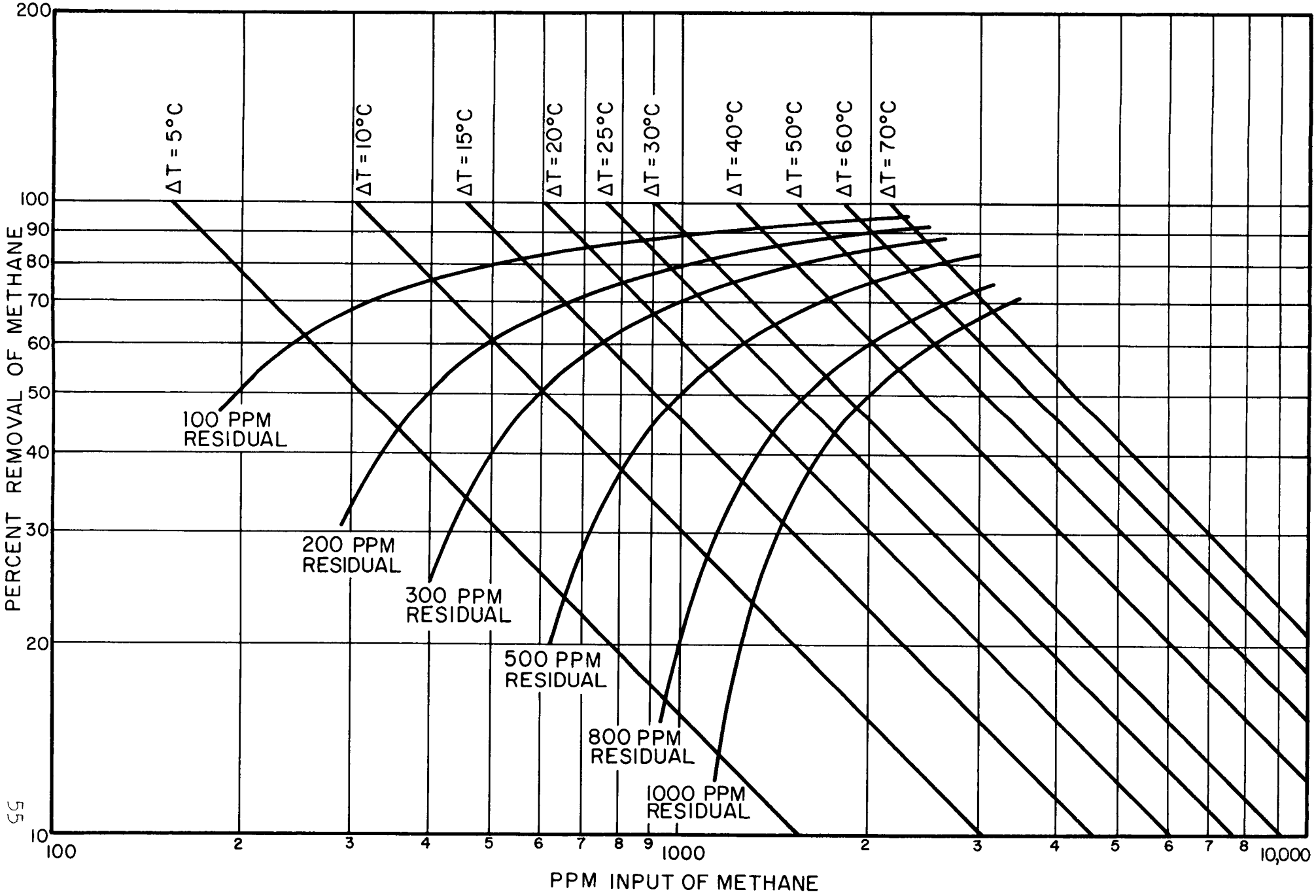

ΔT = 5°C
ΔT = 10°C
ΔT = 15°C
ΔT = 20°C
ΔT = 25°C
ΔT = 30°C
ΔT = 40°C
ΔT = 50°C
ΔT = 60°C
ΔT = 70°C
100 PPM RESIDUAL
200 PPM RESIDUAL
300 PPM RESIDUAL
500 PPM RESIDUAL
800 PPM RESIDUAL
1000 PPM RESIDUAL
PERCENT REMOVAL OF METHANE
200
100
90
80
70
60
50
40
30
20
10
100
2
3
4
5
6
7
8
9
1000
2
3
4
5
6
7
8
10,000
PPM INPUT OF METHANE

FIG. 13

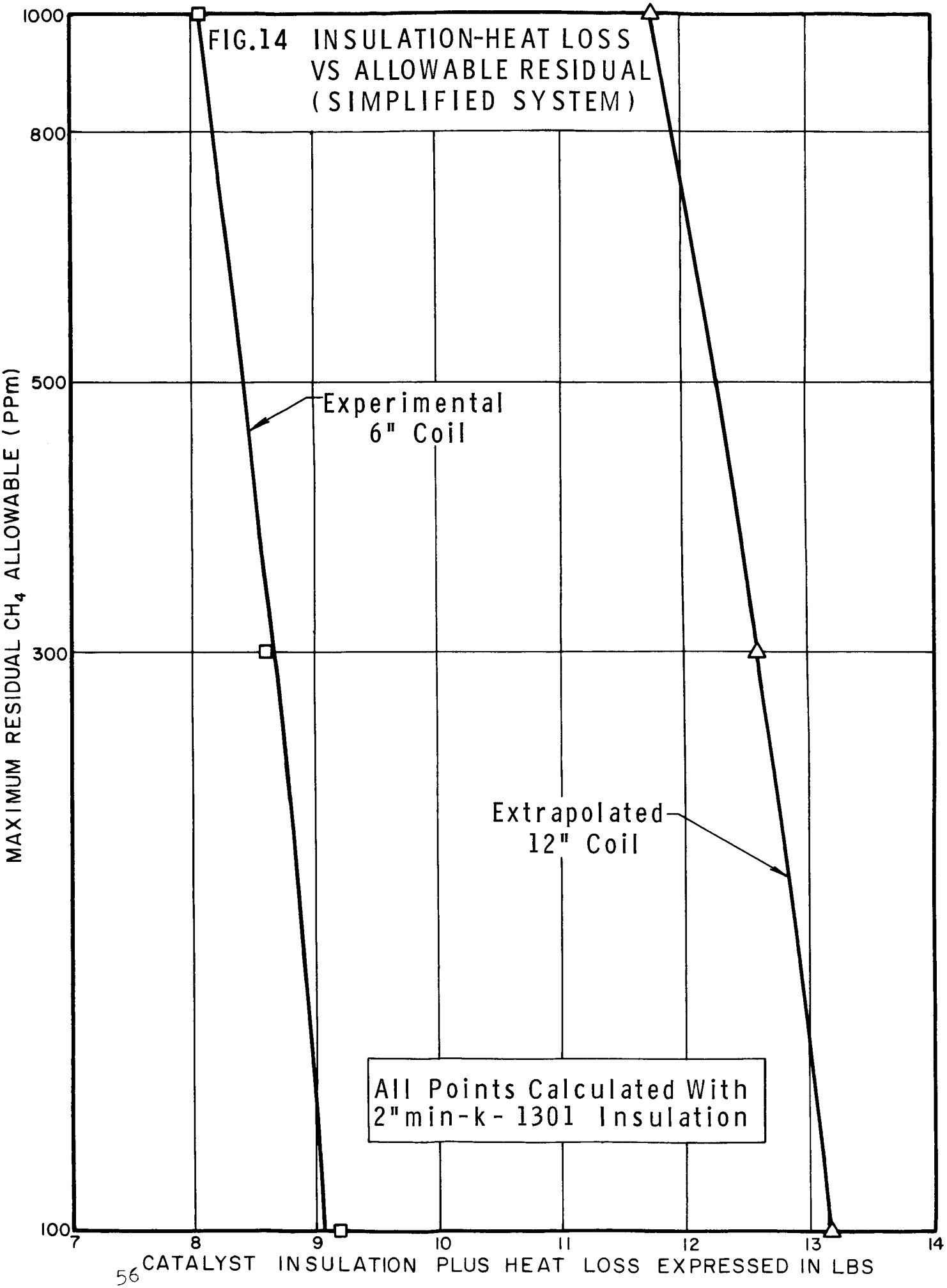
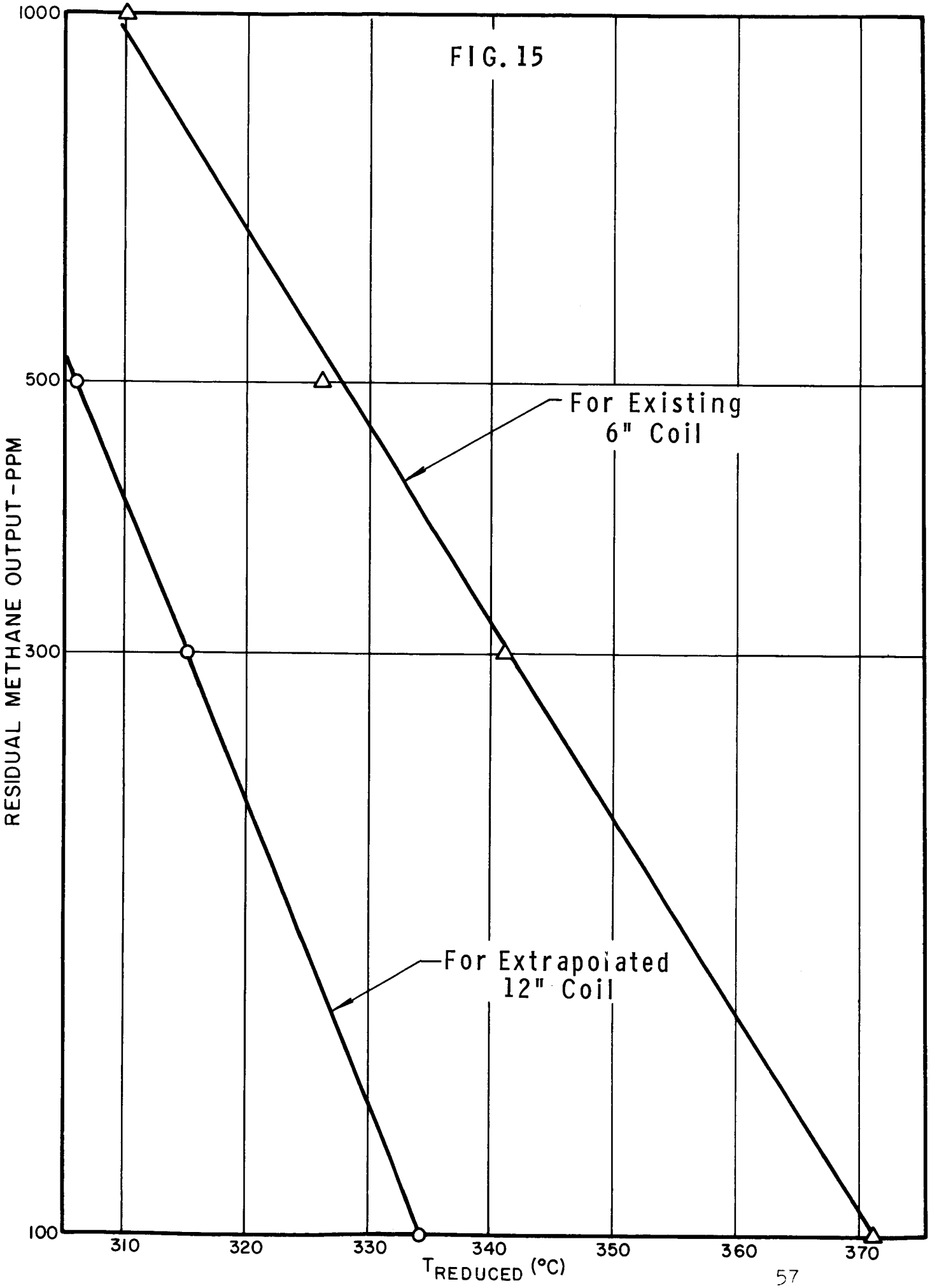


FIG.14 INSULATION-HEAT LOSS VS ALLOWABLE RESIDUAL (SIMPLIFIED SYSTEM)
MAXIMUM RESIDUAL CH_4 ALLOWABLE (PPm)
1000
800
500
300
100
Experimental 6" Coil
Extrapolated 12" Coil
All Points Calculated With 2"min-k-1301 Insulation
7
8
9
10
11
12
13
14
CATALYST INSULATION PLUS HEAT LOSS EXPRESSED IN LBS

FIG. 15


1000
500
300
100
RESIDUAL METHANE OUTPUT-PPM
For Existing
6" Coil
For Extrapolated
12" Coil
310
320
330
340
350
360
370
T REDUCED (°C)

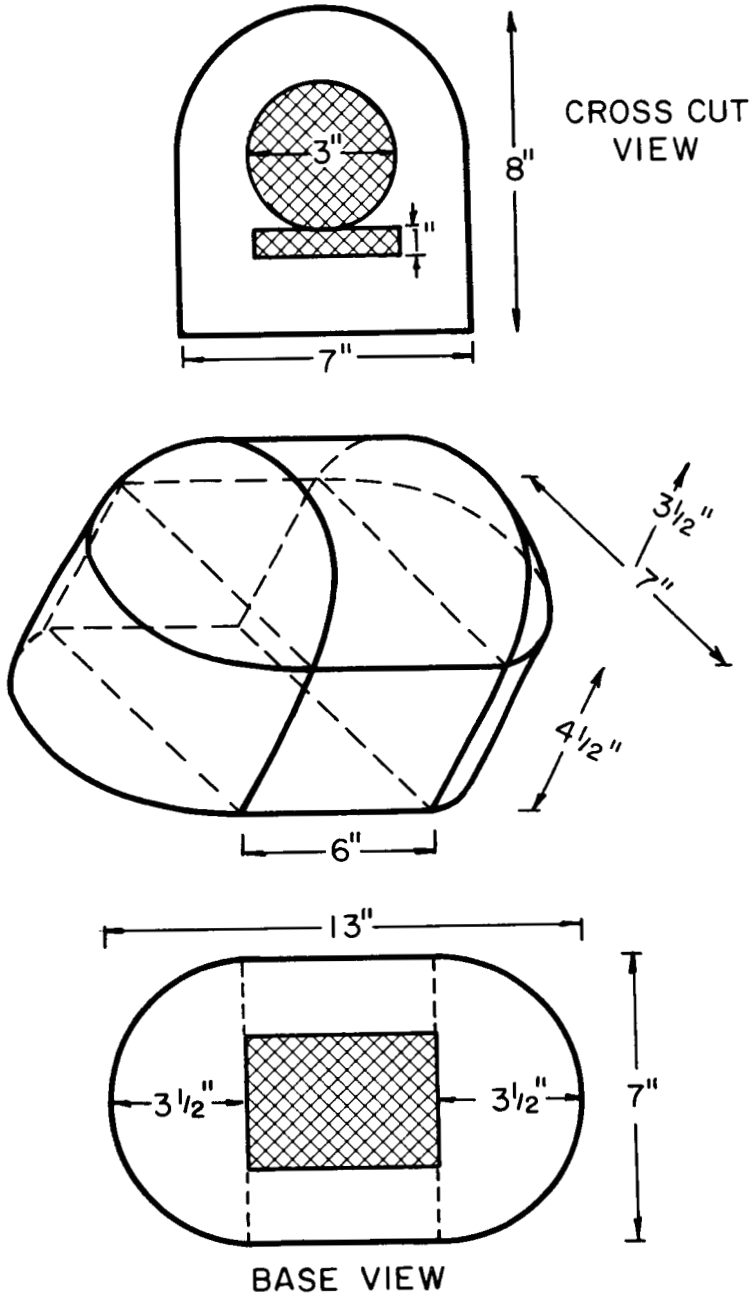


FIG. 16 CATALYST SIZE